Integrated Improvement of Distillation Unit using Multicriteria Decision Making Analysis

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Finally and most importantly, I would like to thank my parents, brothers, and my wife Dewi Yuniasih, for their endless support during my course of study.

Cottbus, October 2006

Er hat den Menschen erschaffen.
Er hat ihm das deutliche Reden beigebracht.
[55:3-4]

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Symbols and notations

Symbols	Description	Unit
$\tilde{a}$	Activity	
A	Area	m^2
$A_{i,j}$	Binary NRTL parameters	$\frac{cal}{mol}$
AC	Annualized cost	-
AF	Annualized factor	-
B	Default basis for weighting factor	-
$B_{i,j}$	Binary NRTL parameters	$\frac{cal}{mol}$
c	Consequence	-
c_p	Heat capacity	$\frac{kJ}{kg \cdot K}$
C	Cost	€
CCF	Capital cost factor	-
d(s)	Disturbances	-
D	Diameter of column	m
EF	Environmental factor	-
EI	Environmental index	-
EP	Economic potential	€
f	Function	-
f	Fugacity	bar
F	Frequency	-
F	Flowrate	$\frac{kg}{s}$
Fc	Correction factor for material, pressure, etc	-
G(s)	Process transfer function matrix	-
Gd(s)	Disturbance transfer function matrix	-
h	Specific enthalpy	$\frac{kJ}{kg}$
h^{∞}	Excess enthalpies	$\frac{J}{mol}$
H	Height of column	m
I	Potential environmental impact	PEI
$\dot{I}$	Rate of potential environmental impact	$\frac{PEI}{h}$
IC	Impact category	-
IP	Impact potential	-
K	Capacity measure	
$\dot{m}$	Mass flowrate	$\frac{kg}{h}$
M	Mass	kg
MLI	Mass loss index	-

MI	Mass index	-
M&S	Marshal and swift index	-
Kc	Controller gain	-
p	Pressure	bar
P	Price	$\frac{€}{year}$
Q	Heat duty	$\frac{J}{s}$
S	Scenario	-
t	Time	h
T	Temperature	K
T_o	Ambient temperature	K
u(s)	Input variables	-
U	Internal energy	J
v	Rating of alternative	-
w	Weighting factor	-
x	Decision variables	-
$\tilde{x}$	Specific molar of liquid	$\frac{mol}{mol}$
X	Mass fraction	wt%
y(s)	Output variables	-
$\tilde{y}$	Specific molar of vapor	$\frac{mol}{mol}$

Greek symbols

α	NRTL parameter
γ	Activity coefficient
γ^{∞}	Activity coefficient at infinite dilution
Δ	Difference
φ	Fugacity coefficient
$\Psi_{n,m}$	UNIFAC/modified UNIFAC (Do) – temperature terms
$\tau_{i,j}$	NRTL parameter

Indices

A	Acetone
B	Base case
c	Impact category
cap	Capital
DT	Distillation tower
e	Energy
E	Equipment
FCI	Fixed capital investment
gen	Generated
HE	Heat exchanger
i,j,l,r	Component indices

in	Input
IRR	Insurance and residual risk
K	Criteria
M	Methanol
n,m	Main groups in UNIFAC groups interaction parameters
N	Tray number
out	Output
p	Product
PE	Purchased equipment
raw	Raw material
S	Stream
SIM	Safety investment and maintenance
SS	Sidestream case
sys	Process system
T	Total
U	Utility
w	Waste
W	Water

Superscripts

α	Exponential value of class membership in ABC classification
L	Liquid phase
M	Constant depending equipment type
T	Transpose matrix
u	Upper matrix
l	Lower matrix
V	Vapour phase
^	Normalized form

Abbreviations

ATP	Aquatic toxicity potential
AP	Acidification potential
BIPs	Binary interaction parameters
CV	Controlled variable
CCA	Cause consequence analysis
ECPD	Environmentally conscious process design
ETA	Event tree analysis
FMEA	Failure mode and effect analysis
FTA	Fault tree analysis
GP	Goal programming
GWP	Global warming potential
HCR	Hydrocarbon recovery
HTPE	Human toxicity potential by exposure
HTPI	Human toxicity potential by ingestion
LC	Level controller
LDF	Light distillate feed stock

LDFT	LDF tank
LLE	Liquid liquid equilibria
LP	Linear programming
LRR	Light residue recovery
MOOP	Multiobjective optimisation programming
MV	Manipulated variable
MCDM	Multicriteria decision making
MILP	Mixed integer linear programming
NLP	Nonlinear programming
OLE	Object link embedded
ODP	Ozone depletion potential
PC	Pressure controller
PI	Proportional integral controller
POCP	Photochemical oxidants creation potential
RPI	Risk potential index
SHE	Safety, health and environment
SQP	Successive quadratic programming
SWOF	Summation of weighted objective function
TC	Temperature controller
TTP	Terrestrial toxicity potential
VLE	Vapour liquid equilibria
WAR	Waste reduction algorithm

Abstract

Stringent safety and environmental regulations, and competitions have challenged the chemical process industries to bring products to market at low lifecycle costs without compromising on safety and environmental standards. Frequently, a large number of alternatives with different structure design and process alternatives of distillation unit can be found to satisfy the demanded criteria of improvement target. Therefore, a systematic method for the improvement of distillation unit is of the considerable interest in order to evaluate the improvement objectives of design alternatives that include economic, environmental and safety criteria. Accordingly, this thesis presents integrated improvement of distillation unit based on careful and simultaneous evaluation of economic, environmental and safety criteria of the design alternatives. The approach for integrated plant improvement in this paper bears the consequence that economically attractive plant might not be the ultimate criteria as the decision tools to choose the best design, but put this economic criteria in a degree of preference in comparison to other criteria. Then, the evaluation of safety and environmental objectives in one side and total cost objectives in other side should be taken into account as a critical step in the plant improvement scenario. This research proposes a fundamental work on evaluation of economic, safety and economic criteria in distillation technology in an integrated manner. Economic evaluation will be calculated based on total annualized cost calculation. Environmental evaluation relies on the calculation of potential environmental impact associated with generated heat and mass balances generated by process simulation. Safety evaluation will be based on dynamic simulation of the investigated distillation unit during disturbance or non-standard operation as well as inherent safety index calculation. At the end, this thesis proposed a methodology for the improvement of distillation unit based on a framework of multi criteria decision making analysis. An analytic hierarchy process methodology is used to support decision upon the criteria for selection, rate the relative importance of the criteria and its advantages/ disadvantages as well as to combine the ratings to obtain an overall rating for each choice of design improvement. The concept will be applied in an existing plant as case study. It is supposed that the proposed integrated-scenario is applicable to support a decision making in chemical industries that always deal all the time with improvement tasks.

1. Introduction

1.1. Background

After past serious accidents in distillation systems, mainly in refinery plant, environmental and safety concerns in distillation and refinery plant have raised public awareness. As a response, there have been number of initiatives and regulations aimed at improving safety level and reducing environmental impact in distillation units.

However, environmentally friendly and safe process might not be the most economical option; it has consequence in increasing plant cost and eventually reduces significant profit. In other words, optimum design with respect to environmental and safety criteria often leads to decreasing economic performance. Therefore, efforts made to compromise two or more decision criteria to achieve an optimum condition are highly expected since the results in a single decision are only efficient in one aspect but inefficient in others.

The optimisation process that consider more than one objective is recognized as multicriteria decision making (MCDM). For chemical industry that deals with stringent regulations and chemical market competition, an effective and efficient decision making process is a key factor for successful business.

Therefore, the intention of this work is dealing with a systematic procedure of multicriteria decision making in distillation column taking into account environmental and safety criteria. Thus, better decision making in optimising distillation column is mostly expected to reduce energy demand, increasing throughput and reducing waste, increase profit and meet regulations compliance.

1.2. Objectives of research

The objectives of this research are:

1. to present theoretical background of multicriteria decision making (MCDM) for optimisation of distillation unit. This MCDM is used an efficient method to trade-off between conflicting objectives that always emerge when optimising design with regard to environment and safety.
2. to develop a multicriteria decision making framework in distillation column taking into account economic, environmental and safety criteria.
3. to support the decision-maker in ranking design alternatives.

1.3. Structure of thesis

Environmental and safety consideration in distillation unit design as well as the explanation on recent problems in improving distillation unit performance are commenced at the beginning of this thesis (chapter I).

Chapter II presents standard design fundamentals based on literature review. It explains the main idea concerning decision making theory and its necessity for chemical industry, and followed by the requirements to fulfill a reliable decision making with particular focus on distillation system considering environmental, safety and controllability criteria.

Chapter III is focused on the decision making aspects that must be taken into consideration in finding the best alternatives. Chapter IV explains fundamental decision criteria for considering an improvement regarding multiple criteria. In addition, the solution approach is described to attain an optimum solution of multicriteria decision.

In chapter V, application of the methodology is demonstrated in a case study. Chapter VI includes conclusion and outlook for further work.

1.4. General review of major contribution

This work is based on methodologies that are discussed in table 1-1. Major contributions in this thesis are:

1. Systematic guidance in conducting environmentally conscious process design and safety assessment and in handling their trade-offs with the economic criteria.
2. Extended models for:
   a. disturbance analysis (models from Jimoh [76] and Can [25], [26] have been extended)
   b. environmental impacts calculation (steady state simulation as well as dynamic simulation are integrated).
3. Systematic methodology of multicriteria decision making for environmental and safety consideration in distillation unit design.

Table 1-1.Comparison of this work with the previous work

Note	**Can** [26]	**Jimoh** [76]	**This Work**
Distillation system	Simple column with binary water – methanol system	Simple column with binary water – methanol system	Complex column with sidestream and with multicomponent system
Improvement of thermodynamic equilibrium simulation	No	No	Yes
Control configuration alternatives	Dual configuration control	Dual configuration control	Dual configuration and sidestream control
Case(s) of disturbance	Cooling water disturbance	Cooling water disturbance	Cooling water, heat source and feed composition disturbances
Simulation tools	gProms	gProms	ASPEN Plus and ASPEN Dynamic
Safety assessment procedure	Failure Mode and Effect Analysis for Plant and Process (FMEA-PP)	None	Following Can's procedure [26]
Discussion about environmental aspects	None	None	Yes, following potential environmental impact assessment
Experimental or verification	Design data from experimental laboratory set up	Design data from experimental laboratory set up	Design and operating data are attained from an existing distillation plant
Discussion regarding optimisation procedures	None	None	Optimisation procedure based on multicriteria analysis framework

2. Standard Design Fundamentals

2.1. Thermodynamic equilibrium

2.1.1. Criteria of selection for thermodynamic models

Reliable phase equilibrium information of the system to be separated is most important for the development, design and optimisation of separation processes. Nowadays, process simulation packages are valuable tools for designing distillation units. Accuracy of process simulation depends strongly on thermodynamic model used. However, many simulations do not reflect what the distillation column is actually doing. Kister [85] reported that about 20% of distillation malfunction were due to mishaps between simulation and real condition of phase behaviour. Misleading simulation associated with incorrect phase behaviour may result in over or under specification and accordingly leads to physical problems like flooding or weeping [84].

Therefore, correctly estimating VLE (and LLE equilibrium) is one important aspect in simulating separation systems. Process simulation is only trustworthy if the thermodynamic model used is applicable. Carlson [27] proposed a practical guidance for selecting a proper thermodynamic model (see figure 2-1).

2.1.2. References of thermodynamic models considered

Vapour and liquid phase are in equilibrium when the fugacities of each component are equal [128]:

$$f_i^V = f_i^L \qquad (2\text{-}1)$$

The fugacity is a function of temperature, pressure and concentration. For the vapour phase a calculation using the fugacity coefficient φ_i is favourable. The coefficient can be derived from a constitutive equation for the vapour phase:

$$\varphi_i = \frac{f_i^V}{\tilde{y}_i \cdot p} \qquad (2\text{-}2)$$

For ideal gas or gases at moderate pressure, the coefficient can be neglected, that is: $\varphi_i = 1$.

The fugacity of liquid phase can be calculated by the use of the activity coefficient γ_i:

$$\gamma_i = \frac{\tilde{a}_i}{\tilde{x}_i} = \frac{f_i^L}{\tilde{x}_i \cdot f_i^0} \qquad (2\text{-}3)$$

The activity coefficient can be derived by excess enthalpy models like WILSON, or NRTL [58]. The standard fugacity f_i^0 can be exchanged by the vapour-pressure p_i^0 since for

moderate pressures and non-compressible liquids the fugacity coefficient and the pointing-factor are close to equal one. The calculation of the phase equilibrium is as follows:

$$\tilde{y}_i \cdot p = \gamma_i \cdot \tilde{x}_i \cdot p_i^0 \qquad (2\text{-}4)$$

For the calculation of the activity coefficient γ_i, there are some suitable activity coefficient models for the vapour-liquid behaviour of nonideal mixture available. For recent application, the group contribution models have become increasingly valuable since experimental data are often missing or of poor quality. The great advantage of the group contribution concept is that it is possible to predict a large number of systems using only a relatively small number of group interaction parameters. The most common group contribution methods for the prediction of phase equilibrium were explained in Gmehling [58].

The NRTL (Non Random Two Liquid) model uses three binary interaction parameters (BIPs) for each binary pair in a multicomponent mixture. There are N(N-1)/2 such molecular binary pairs for an N component system. For calculation of activity coefficient, the NRTL equation was used to extend the Wilson equation in following formulation:

$$\ln \gamma_i(T,\tilde{x}) = 1 - \ln\left(\sum_j \tilde{x}_j \cdot \Lambda_{i,j}\right) - \sum_k \frac{\tilde{x}_k \cdot \Lambda_{k,i}}{\sum_j \tilde{x}_j \cdot \Lambda_{k,j}} \qquad (2\text{-}5)$$

where :

$$\Lambda_{i,j} = \exp\left(a_{i,j} + \frac{b_{i,j}}{T} + c_{i,j} \cdot \ln(T) + d_{i,j} \cdot T\right)$$

i,j = component indices

The parameters of $a_{i,j}$ to $d_{i,j}$ can be found from thermodynamic parameters of vapour liquid data collection [56] and are available within ASPEN thermodynamic data bank.

In recent years, modified UNIFAC (Dortmund) has become very popular because of its reliable results obtained for different thermodynamic properties such as VLE, SLE, LLE, azeotropic data, activity coefficient at infinite dilution (γ^∞) and excess enthalpies (h^∞) in a wide temperature range [57],[58],[59].

One of the main differences between original UNIFAC and Modified UNIFAC (Do) is the introduction of temperature dependent interaction parameters to permit a more reliable description of the real phase behaviour as a function of temperature [57]:

Original UNIFAC :

$$\Psi_{nm} = \exp\left[-\frac{a_{nm}}{T}\right] \qquad (2\text{-}6)$$

Modified UNIFAC (Do):

$$\Psi_{nm} = \exp\left[-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right] \qquad (2\text{-}7)$$

One possibility to obtain the required information regarding thermodynamic phase equilibrium behaviour is to carry out measurements for the pure compounds and mixtures of interest. However, measurement are time consuming and therefore expensive. For a 10-component system and with 10 % mole-steps the 92378 associated data measurements will

take 37 years [58]. For practical purposes, sources of VLE and LLE data are possibly obtained from Sorensen and Arlt book [125], Azeotropic data banks and DECHEMA Thermodynamic Data Bank. Therefore, the development, optimisation and simulation of chemical plants are usually carried out using the attractiveness of commercial process simulator like ASPEN Plus in order to obtain the required phase equilibrium data. A strategy to improve phase equilibria with NRTL and UNIFAC (Do) models was proposed by Suhendra [131],[132],[133].

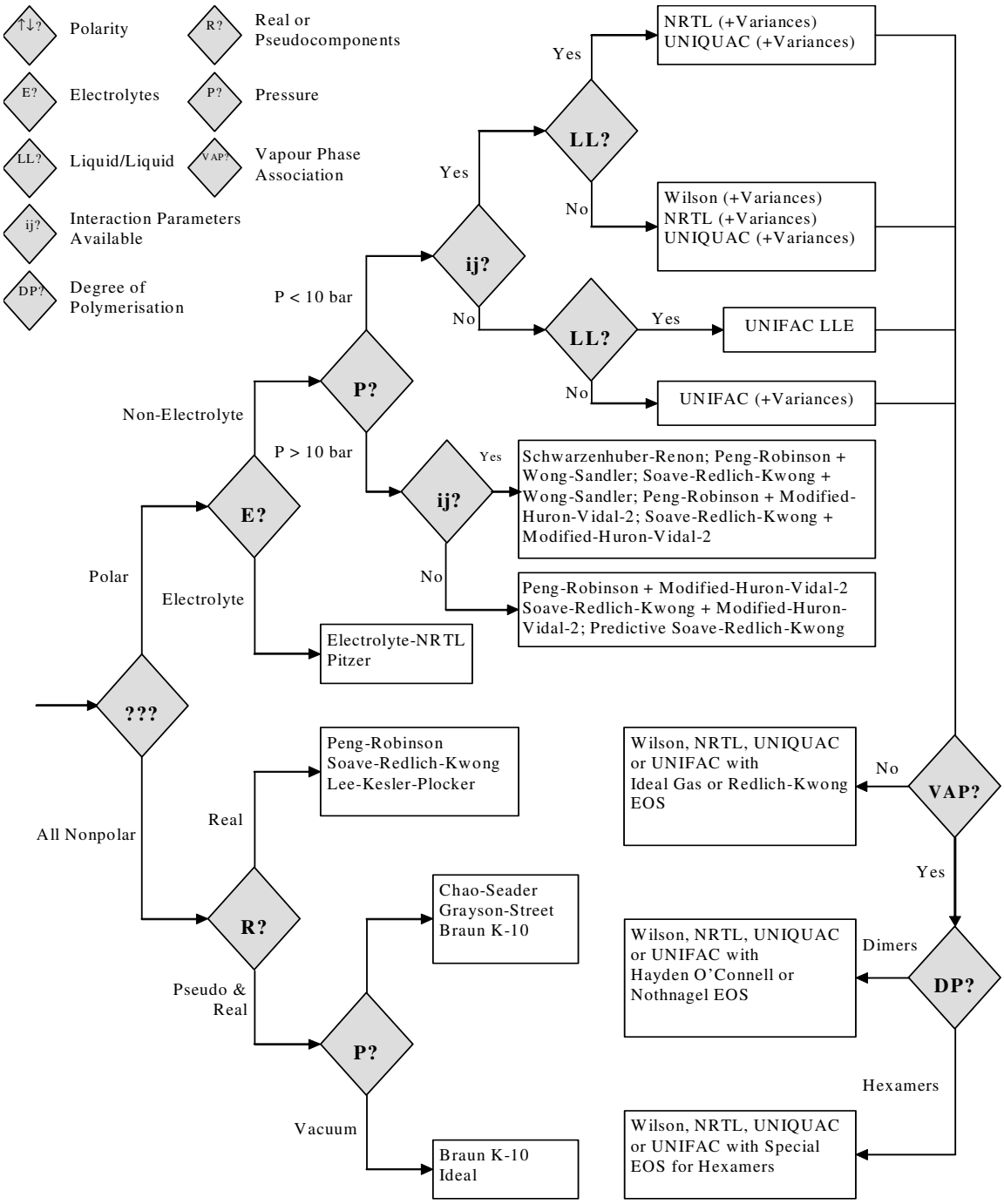


Figure 2-1. Decision tree for the systematic choice of thermodynamic models from process simulators [27].

2.2. Aspects of multicomponent distillation

2.2.1. Arrangements of distillation units

The arrangement of multicomponent distillation systems has been studied by many workers. Simple and complex column configurations have been analysed. Simple configuration refers to the sequences of conventional one-feed, two-product columns, while complex configurations refers to sequences of columns with at least one column having more than one feed and/or more than two products.

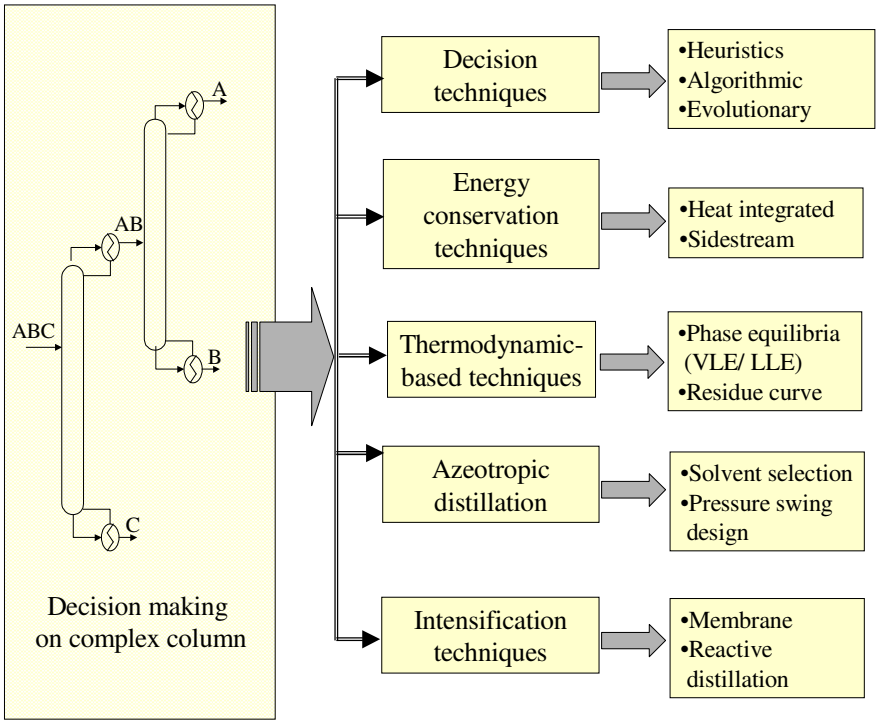


Figure 2-2. Aspects considered for decision making in designing complex column

Some different aspects were considered in order to get better decision in designing complex column as shown in the figure 2-2 above. The first aspect, the improvement technique, deals mainly with three techniques to get an optimum condition in synthesising complex distillation, namely:

(1) heuristics or "rules of thumb" which have been established mainly to reduce the number of schemes to be studied,
(2) algorithmic techniques in which optimisation methods are used, and
(3) evolutionary strategies where both heuristics and algorithmic techniques are combined.

Heuristics provides “a rule” for approximating the ultimate optimal sequence, while algorithmic techniques rely on mathematic approach based on optimisation algorithm. The optimisation algorithm in the field of process engineering will be discussed in the next section.

Normally, minimisation of energy consumption in the required separation can be obtained by arranging the columns in an optimised sequence. These columns can be put

together in a number of ways. However, in order to reduce some of the sequences alternatives, some rules of thumb have been proposed. Douglas [44] proposed synthesis design procedure in order to minimise waste in chemical processes, mainly in separation processes.

Following section will discuss energy conservation and thermodynamic aspects in distillation column, whereas other two aspects, azeotropic distillation and intensification techniques are more specific aspects in distillation research and therefore beyond the discussion in this thesis.

However, the reader is suggested to refer Tsouris and Procelli [137] for the new developed technologies called process intensification. The discussion covers the new developed technologies that replace large, expensive, energy-intensive, or normally called as process intensification with smaller, less costly and efficient one. Furthermore, special issue on reactive distillation was elaborated by Sundmacher [135]. Whereas, intensive studies from Dennis, Thong and Jonson [37], [38], [39] and Kival, Hilmen and Skogestad [88] can be read for azeotropic distillation references.

2.2.2. Energy conservation

Due to the fact that distillation is a highly energy intensive process, energy consumption is a critical issue in designing and operating this unit. Previous researches to conserve energy in distillation columns concluded that it is economic to use sidestream column if product purity is moderate to low [3], [48], [53], [54]. In essence, the main objective of this sidestream column is to purge small amounts of impurity.

Most of the application of previous research in sidestream has considered only a system containing three components with decreasing order of volatilities: let say, A, B and C. Then, sidestream column is often used in case with very small amounts of either the lightest component or the heaviest component. According to Glinos and Malone [53] and Luyben W., Tyreus and Luyben M. [105], the rule of thumb for phase condition and tray location relationship of sidestream are represented in figure 2-3 below.

From figure 2-3, the design criteria of sidestream location depends on whether the sidestream is below or above the feed tray and on whether it is taken off as a vapour or as a liquid. It is suggested the liquid above and the vapour below the feed (configuration 1 and configuration 2 respectively) are the richest in the middle component [53]. But there is also incentive for taking a liquid sidestream below the feed (configuration 3). Liquid sidestream may lose in purity but the vapour rate required is drastically reduced and therefore the column is cheaper. The fourth possibility is a vapour sidestream above the feed (configuration 4). Since there are no savings in vapour rate, a lower maximum concentration of middle component and few applications we are aware of, this alternative is not considered.

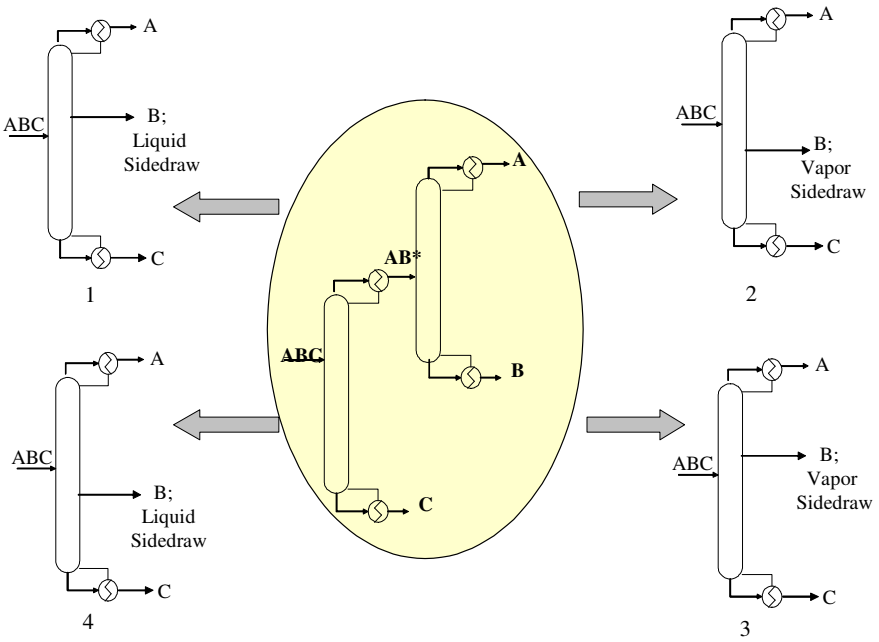


Figure 2-3. Configuration alternatives for minimising energy consumption using sidestream.

In order to improve the purity of sidestream, three design alternatives were introduced namely sidestream with small stripper (SS), small rectifier (SR) and prefractionator (PF) respectively [53]. In the SS, liquid sidestream is fed in the top of stripping column. This stripping column has a small reboiler to strip out the lightest component. While, in the RS the vapour sidestream is fed in the base of rectifying column to remove some of the heaviest component in the vapour stream. The last one, prefractionator column, consists of prefractionator to perform a rough separation and followed by the final separation into three products stream in a two-feed sidestream column.

Other attractive complex column configurations for energy conservation purposes are namely Petlyuk column or divided wall column and heat integrated distillation column. Employing complex column configurations can minimise these mixing losses, as well as reduce energy consumption and decrease capital costs. Such columns promote greater interaction between vapour and liquid streams by introducing thermal coupling between different sections. Columns are thermally coupled together, and can result in a second column being forced to run at the same pressure as a first one to which it is thermally coupled. This creates a balance between the ease of separation (relative volatility) and the reflux ratio. Some configuration alternatives are shown in the figure below. Illustration of some alternatives configurations of heat integrated distillation column are shown in figure 2-4.

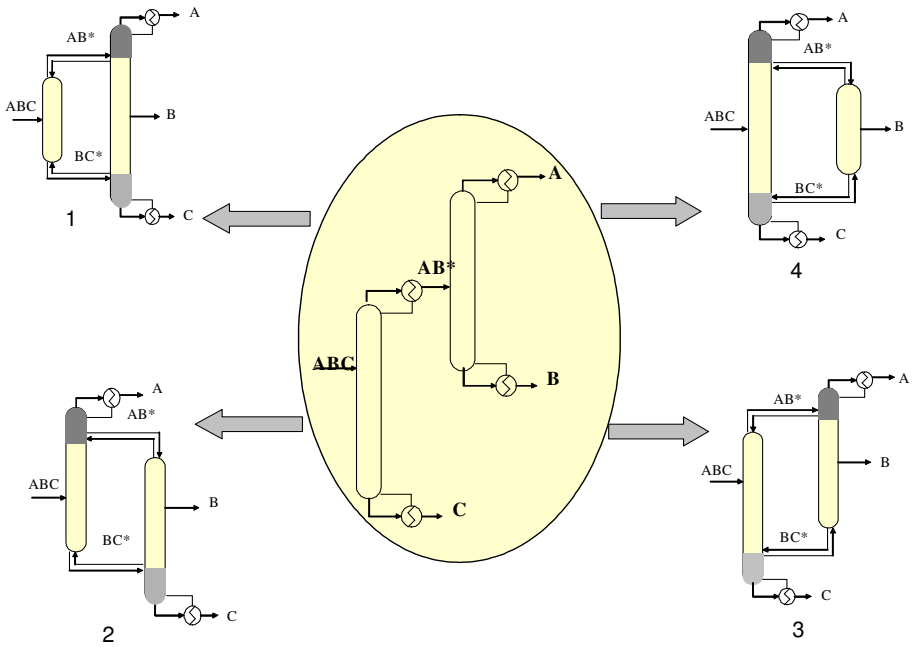
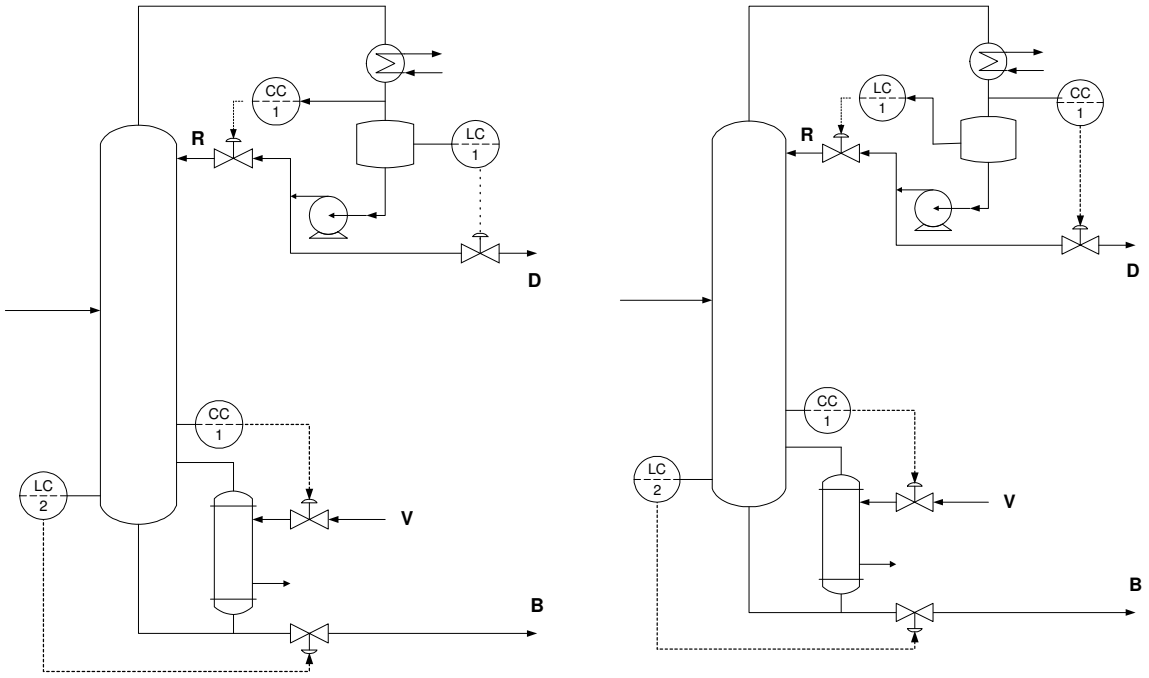


Figure 2-4. Configuration alternatives for heat integrated distillation column

2.2.3. Control configuration

Some alternatives of common control configuration in distillation are shown in table 2-1. For a simple distillation column, energy consumption is minimised when both products are held at specified purities. Therefore, from a steady-state energy consumption standpoint, it is desirable simultaneously to control both product compositions in a distillation column. This is called “dual composition control”. Typical configurations of dual composition control are depicted in figure 2-5.



(a) RV configuration (b) DV configuration

Figure 2-5.Typical configurations of dual composition control: (a) RV configuration, (b) DV configuration. CC and LC represent composition and level controls respectively [105].

Table 2-1. Description of typical control configuration in distillation column [105].

Control configuration	Properties and explanation
RV	Reflux flow controls distillate composition, heat input controls bottom's composition. It usually handles feed composition changes quite well
DV	Used in a high reflux ratio because the distillate flowrate is too small to control reflux drum level.
RR-V	Reflux ratio is used to control distillate composition and heat input controls bottom compositions
R-B	When the boilup ratio (V/B) is high, bottoms flow should also be used to control bottoms composition and heat input should control the base level. However, in some columns potential inverse may create problems in controlling base level with boilup
RR-BR	Reflux ratio controls distillate composition and boilup ratio controls bottom composition.

Note: R: reflux rate, V: boilup rate; D : distillate rate; RR: reflux ratio; BR: boilup ratio

However, dual composition control can lead to dynamic control problems. Interaction between the two composition control loops can result in closed-loop stability difficulties. Instrumentation complexity and cost increase if interaction compensators (decouplers) are required. Engineering costs are also significantly increased if dynamic simulation studies, detailed control system design, and/or plant tests are required [105].

It is important to note also that dual composition control is not needed to minimise energy consumption when feed rate changes occur. Throughput disturbances can be simply handled by rationing reflux or heat input to feed rate while controlling one product composition. Feed composition variations are the principal disturbances that require a dual composition control system in order to minimise energy consumption. Therefore the energy savings of dual composition control must come primarily from achieving the minimum vapour boil-up/feed ratio (V*/F)* as feed composition disturbances are encountered [82].

Due to very significant reductions in energy consumption complex configurations, chemical industry uses columns with multiple feeds, sidestreams, combinations of columns, and heat integration to improve the efficiency of the separation processes. However, they present more challenging control problems. Side products complicate column control [103].

Technically, each side product adds two control variables (side product lights and heaviest concentrations) but only one manipulated stream (side product flow) to the column. Only one of these two compositions can be controlled by the additional manipulated stream; the other is allowed to vary or rides on the nearest end product composition. Alternatively, both lights and heavies content of the side product can be controlled, at the expense of letting the composition of one of the end products vary. Side draw offs, in addition, also escalate the potential for interaction among control loops [17].

Typical configurations of sidestream control are depicted in the figure 2-6 below. These configurations, controlling sidestream via temperature control and ratio control respectively, were discussed already by Luyben [99], [100], [105], [106] and elsewhere [3], [17], [53], [54].

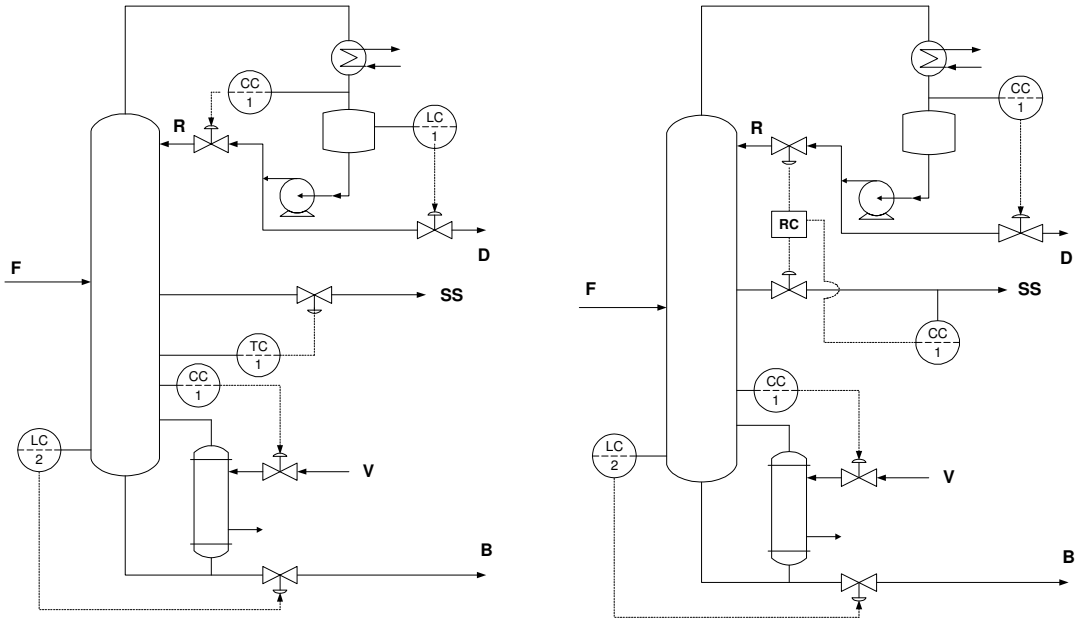


Figure 2-6. Configuration alternatives for sidestream control (a) using temperature control; (b) using ratio control [105] .

2.3. Rigorous dynamic model of distillation column

The development of dynamic model of distillation column begins with the evaluation of the balance equations (e.g. energy and mass balances). It takes also into account that one part of distillation column will be liquid mass and the other part is vapour mass [76].

Consider the i^{th} tray of the column as shown in the figure 2-7 below. The mass balance for this tray is:

$$\frac{dM^{tot}}{dt} = F_{in}^{L} + F_{in}^{V} + F_{Feed} - F_{out}^{L} - F_{out}^{V} \qquad (2\text{-}8)$$

Where the total mass holdup of the tray, M^{tot}, comes from the sum of liquid and vapour holdup:

$$M^{tot} = M^{L} + M^{V} \qquad (2\text{-}9)$$

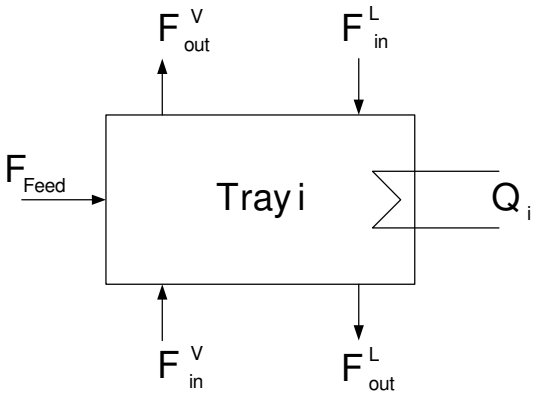


Figure 2-7. Common distillation tray for modelling mass and energy balance

Different operating conditions at the column lead to different hold up. Analogously, the component mass balance of that tray can be composed as:

$$\frac{dM_i}{dt} = F_{in}^{L} \cdot x_{i,in} + F_{in}^{V} \cdot y_{i,in} + F_{Feed} \cdot z_{Feed} - F_{out}^{L} \cdot x_{i,out} - F_{out}^{V} \cdot y_{i,out} \qquad (2\text{-}10)$$

with the hold up of component i in both phases:

$$M_i^{tot} = M^{L} \cdot x_i + M^{V} \cdot y_i \qquad (2\text{-}11)$$

Furthermore, the energy balance of the tray can be formulated as:

$$\frac{dU}{dt} = F_{in}^{L} \cdot h_{in}^{L} + F_{in}^{V} \cdot h_{in}^{V} + F_{Feed} \cdot h_{Feed} - F_{out}^{L} \cdot h^{L} - F_{out}^{V} \cdot h^{V} \qquad (2\text{-}12)$$

where the total energy is formulated as:

$$U = M^L \cdot h^L + M^V \cdot h^V - p \cdot V_{tray}^V \quad (2\text{-}13)$$

where the enthalpy of liquid or vapour phase is

$$h^L = h^L(p,T,x);\ h^V = h^V(p,T,x) \quad (2\text{-}14)$$

and V_{tray}^V is:

$$V_{tray}^V = M^V \cdot \bar{v}^V \quad (2\text{-}15)$$

and specific volume of liquid or vapour:

$$\bar{v}^L = \bar{v}^L(p,T,x);\ \bar{v}^V = \bar{v}^V(p,T,x) \quad (2\text{-}16)$$

For the representation of column efficiency, Murphree efficiency is used:

$$\eta_i = \frac{\tilde{y}_{i,out} - \tilde{y}_{i,in}}{\tilde{y}_i^* - \tilde{y}_{i,in}} \quad (2\text{-}17)$$

The composition (mol fraction), $\tilde{y}_i^*$, may be calculated via equation of state:

$$\varphi_i^V \cdot \tilde{y}_i^* = \varphi_i^L \cdot \tilde{x}_i \quad (2\text{-}18)$$

where φ_i^V and φ_i^L represent the fugacity coefficients of component i at vapour and liquid phase, respectively.

$$\varphi_i^V \cdot p \cdot \tilde{y}_i^* = \varphi_i^L \cdot \tilde{x}_i \cdot p_{0,i} \quad (2\text{-}19)$$

Further, the sum of all mole fractions must be 1:

$$\sum_{i=1}^{Ncomp} y_i = 1;\ \sum_{i=1}^{Ncomp} y_i^* = 1 \quad (2\text{-}20)$$

3. Decision Making Aspects

3.1. Decision making process

3.1.1. The need of decision making in chemical process

Decision making is the process of definition and selection a possible set of parameters from all the available alternatives. Chemical engineers are decision makers because they always deal with the activities to select any possible action to achieve the best alternatives, e.g. the improved design processes.

To carry out the goals, chemical engineers must have an understanding of all relevant aspects. Reasons for decision making in chemical industries are:

1. Plant management routinely face decision making problems when they have to make annual decisions on whether and by how much to expand manufacturing capacity and monthly decision on how much product to make.
2. Plant management have to trade-off between possible profit will be obtained and annual/monthly risk will be occurred that must be taken and possibly could cause them to go out of business.
3. Plant management always deal with reduction of energy consumption all the time due to the vulnerability of energy supply world wide. Reducing energy consumption in chemical industrial will reduce the expenses as well as reduce environmental impacts. The cost for reducing energy should be compromised with the expense of the best available energy conservation.
4. Plant management requires an improvement of technology in use to survive their business by producing high quality of products and services and accordingly increasing corporate image and profit. The selection of technology for improving chemical plant performance must be decided with regard technical, social and economic aspects.
5. Plant management must record product quality improvement to meet customer expectations. The quality must be monitored through tight control management.

Therefore, effective and efficient decision making decision making processes in chemical industries are key factors for successful in chemical business entrepreneurships. However, environmentally friendly and safe process might not be the most economical option; it may have consequence in increasing plant cost and eventually reduces significant profit. In other words, optimum design with respect to environmental and safety criteria often leads to decreasing economic performance. Therefore, efforts made to compromise two or more decision criteria to achieve an optimum condition are highly expected since the result of a single criteria decision might be only efficient in one aspect but inefficient in others. The optimisation process that consider more than one objective is recognized as multicriteria decision making (MCDM) [68].

3.1.2. Steps in decision making process

According to Heizer and Render [68], a good decision follows six steps as shown in figure 3-1. In the first step, problem definition, the problems are stated clearly and concisely, which in many cases is the most important and difficult step.

In the second step, criteria and goals establishment, managers must develop specific and measurable objectives. Most firms have more than just the goal of maximising profit.

In the third step, model formulation, a representation of the situation - a model has to be developed. Models can consist of either one variable or more. A variable is the measurable quantity that may vary or is subject to change.

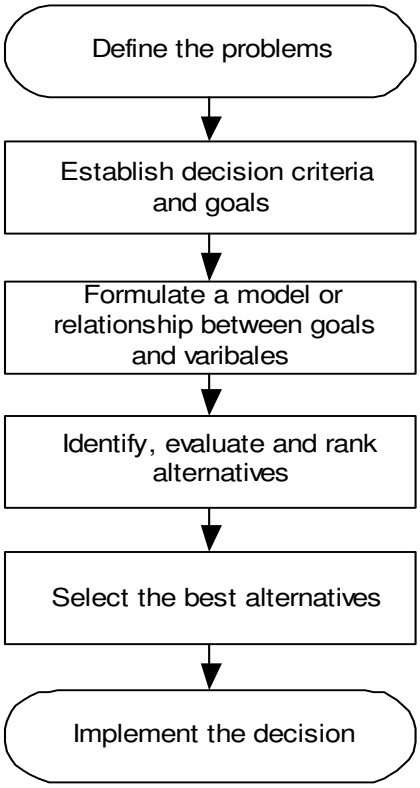


Figure 3-1. Six steps of decision making [68]

The forth step, alternative identification and evaluation, means that generating as many solutions to the problems as possible (and usually quickly). A range or set of options is what most managers like to have. The evaluation should result in a ranking of preference according to the desired criteria.

The fifth step is the best alternatives selection meaning that deciding the solution that best satisfies and most consistent with the stated goals.

And eventually, in the last step, the decision implementation, the actions are carried out regarding selected alternative. It involves task assignments and a timetable for implementation.

3.2. Sensitivity analysis and parameter optimisation

3.2.1. Sensitivity analysis in process simulators

One of the main approaches exists for process modelling is the sequential modular approach, such as ASPEN Plus. In this modular approach, the user can construct the process flowsheet model, typically with a user-friendly graphical interface, by connecting blocks corresponding to members of a library of unit operation model subroutines. The simulator then analyzes the flowsheet structure and solves the problem with an appropriate algorithm. The unit operation model libraries typically contain collections of subroutines implemented in particular programming languages such as C or Fortran. Information moves through the flowsheet model consisting unit operations models in a similar manner to the material flow through the actual process, from the output of one unit operation to the input of the next, and so on. The structure of such simulator is shown in the figure 3-2.

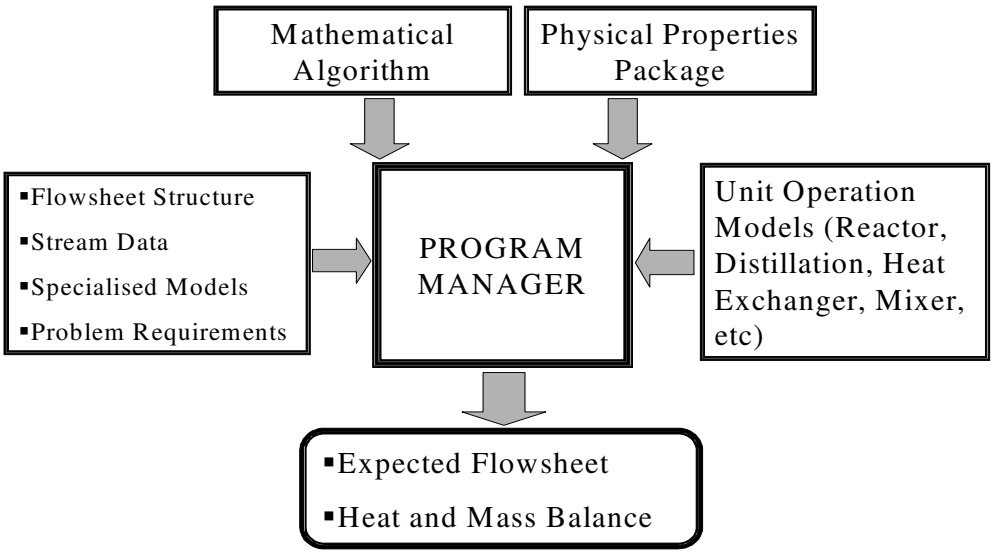


Figure 3-2. Organisation of modular simulator

A black box characteristic in ASPEN Plus is emerged since the objective function is unknown and mathematical procedure therefore cannot be applied. Therefore, an alternative method is made by applying different initial guess and verifying the same answer is obtained [37].

One of the important features in the sequential modular approach is the sensitivity analysis capability. Sensitivity analysis consists of analyzing the response of dependent variables of a process with respect to a change of decision variables. With the use of this simulator, sensitivity analysis is directly performed on a process simulation model. Decision variables physically represent equipment specifications and operating conditions while dependent variables are the outcome to be affected [41].

However, due to such structure, the model equations inside the unit operations in sequential modular process simulators are most often not accessible. Therefore, problem variables have to be *perturbed* around their base case values and the corresponding operating steady-states of the process model have to be calculated at each perturbation accordingly [41].

Therefore, two common approaches in sensitivity analysis are [41]:

- Analytical differentiation. This approach is used if models are represented exactly.
- Perturbation. This approach is used if models are not represented exactly.

The sensitivity analysis is important for the application for [18]:

- determination of control structure
- reduction of optimisation procedure
- experimental modelling assessment for modelling
- uncertainty and robustness assessment.

3.2.2. Parameter optimisation in process simulators

If the process optimisation only concentrates on problem variables that can be varied continuously in a region (process operating parameters) and can thus be solved by non-linear programming, the case is referred to as *parameter optimisation* [18].

ASPEN Plus maximises or minimises a user-specified objective function by manipulating decision variables (feed stream, block input, or other input variables). The objective function can be any valid Fortran expression involving one or more flowsheet quantities. The tolerance of the objective function is the tolerance of the convergence block associated with the optimisation problem. There is also an option in imposing equality or inequality constraints on the optimisation. Equality constraints within an optimisation are similar to design specifications. The constraints can be any function of flowsheet variables computed using Fortran expressions or in-line Fortran statements [42].

In a process simulator the constraint equations are included in the process simulation model itself. Problem variables are further classified into *decision variables* that represent degrees of freedom in the optimisation and dependent variables that can be solved from the constraint equations. Often, the optimisation problem for a chemical process has a non-linear objective function and/or non-linear constraint equations of the problem variables and is referred to as *non-linear program*. The solution of this kind of optimisation problems is referred to as *non-linear programming* (NLP) [41].

There are numerous algorithms to solve non-linear problems in both sequential modular and equation-oriented process simulators. Successive Quadratic Programming (SQP) is one of the most frequently used algorithms in both types of simulators as it requires far fewer calculation steps than other well-known methods [14]. The SQP-algorithm is implemented in the Aspen Plus® software package and is used for the parameter optimisation [42]. Furthermore, the use of optimisation programme in ASPEN Plus is described in table 3-1, including the optimisation features and their application in ASPEN Plus.

The integration of ASPEN Plus as decision support tool for design and process selection has been introduced by Kheawhom and Hiraou [78], [79]. The illustration of the working concept is shown in figure 3-3 below. The SQP optimisation algorithm is built within Aspen Plus™ and is used for environmental and economic optimisation of each alternative. With the object link embedded (OLE) of the ActiveX technology, the interaction between Aspen Plus and a programming interface such as Microsoft Visual Basic is carried out. While, a data manager from Excel Spreadsheet is used as working platform for economic, environmental and safety models.

Table 3-1. Explanation of the application of optimisation in ASPEN Plus

Optimisation Features	Application in ASPEN Plus
Maximising/ Minimising Objective Function Approaches	By manipulating decision variables (feed stream, block input, or other input variables
Kinds of Objective Function	Any valid Fortran expression involving one or more flowsheet quantities
Tolerance	The tolerance of the convergence block associated with the optimisation problem
Constraints	Equality constraints within an optimisation are similar to design specifications. The constraints can be any function of flowsheet variables computed using Fortran expressions or in-line Fortran statements
Tear streams	Can be converged simultaneously or separately.
Algorithms	The COMPLEX method and the SQP method
Convergence	Solves optimisation problems iteratively. By default Aspen Plus generates and sequences a convergence block for the optimisation problem
Variables in simulation	Those are entered by user: These variables may be either read or written. Those are calculated by ASPEN Plus: These variables should only be read.
Recommended procedure	Start with a simulation Perform sensitivity analysis before optimisation Evaluate the solution using sensitivity analysis

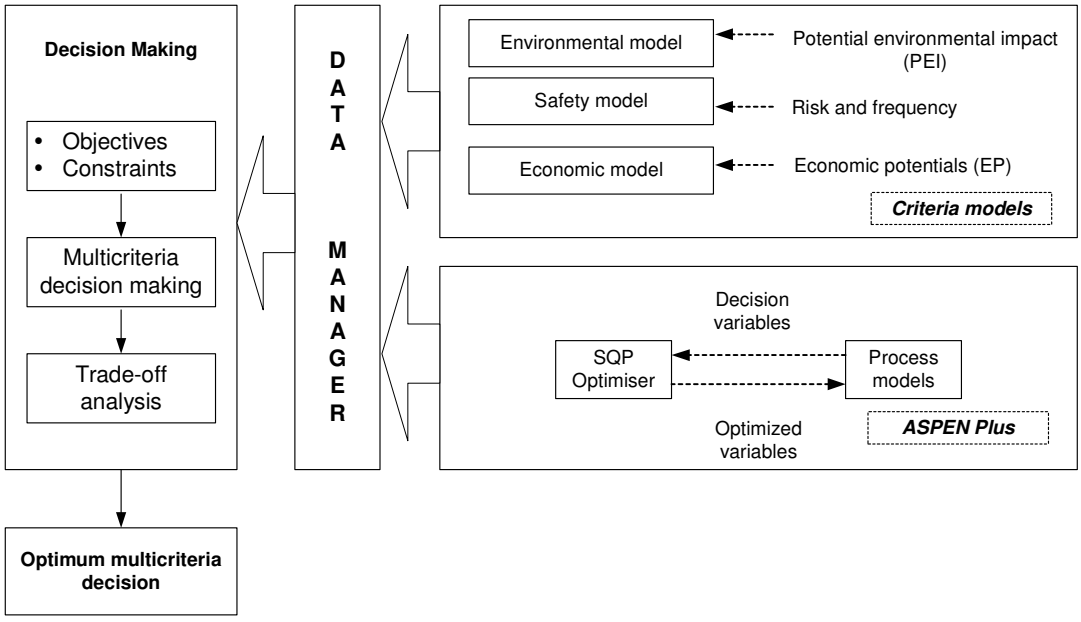


Figure 3-3. The concept of multicriteria optimisation using ASPEN Plus [78]

3.2.3. Dynamic simulation of plant disturbances

Generally, the goals of dynamic simulation for safety-related assessment are [26]:

- Assessment of physical effects of disturbance in the plant
- Evaluation of possible malfunctions associated with the particular disturbance
- Technical know-how for relevant disturbances and associated effects, as well as risk on economy and emission
- Assessing alternatives for system optimisation
- Assessing system protection.

For distillation column, the goals, for instance, are:

- interpretation of the pressure relief area and pressure response of relief valve.
- evaluation of the forces affecting with a disturbance on the trays
- estimation of the steam mass flows and increase of pressure speeds.

The coverage in dynamic simulation, therefore, will emphasize following operational aspects: what various control schemes can and cannot do, how to put together a control system, how to recognize and avoid a troublesome system, what are the ill effects of various poor control schemes, and what corrective action can restore trouble-free operation [106].

3.3. Optimisation methodologies

3.3.1. Classification of optimisation methodologies

Optimisation means attempts to achieve the best condition from some alternatives. In chemical processes, optimisation has a target mainly to obtain significant reduction in plant cost thus improve plant profit. Edgar and Himmelblau [46] explained detail issues on optimisation in chemical process. From mathematical viewpoint the optimisation means to find minimum or maximum value of the objective function subject to constraints. The optimisation problem is often formulated mathematically by following statement:

Minimise/ Maximise $f(\mathbf{x})$ (3-1)

with respect to: $\mathbf{x} = (x_1, x_2, \ldots, x_n)$

subject to the constraints:

$h_i(x) = 0 \qquad i = 0,1,2,\ldots, m$

$g_j(x) \leq 0 \qquad j = 0,1,2,\ldots, n$

where: x : set of independent variables,

$f(x)$: objective function,

$h_i(x)$: equality constraint functions,

$g_j(x)$: inequality constraint functions.

In practical terms, optimisation is performed on a given process in order to quantify its "best solution" with respect to a quantitative performance measure, called as the *objective function*. Typical objectives for process optimisation include e.g. the minimisation of process capital costs and the minimisation of variable process costs. The values of the objective function are determined by manipulation of the problem variables. Further, limits of process operation and product quality specifications, process safety limits, and relationships between

the problem variables need to be considered as *constraint equations*. These constraints can be either the equality or inequality functions [43].

In general, most common targets to be optimized in chemical process optimisation are:

- minimisation of fuel consumption
- minimisation of exergy destruction
- minimisation of emitted pollutants
- maximisation of the internal rate of return (IRR)
- minimisation of the payback period (PBP)
- minimisation of incident-risk

Most of optimisation topics in Himelblau's book [46] considered single objective only, mainly considering economic or design objectives. Important techniques in this single objective optimisation are linear programming (LP), non-linear programming (NLP), integer programming (IP), mixed integer linear programming (MILP) and mixed integer non-linear programming (MINLP).

However, if the problem consists of two ore more conflicting objectives, the problem is then classified as multiobjective optimisation. The difference between single objective and multi objective optimisation in mathematical expression is illustrated in figure 3-4 below.

It is shown from figure 3-4 that the use of multiobjective optimisation aims to solve two or more objectives. The need on multiobjective optimisation rises mainly due to the existence of some conflicting objectives in single optimisation technique. Some methodologies for solving multiobjective optimisation problem will be discussed briefly in the next section.

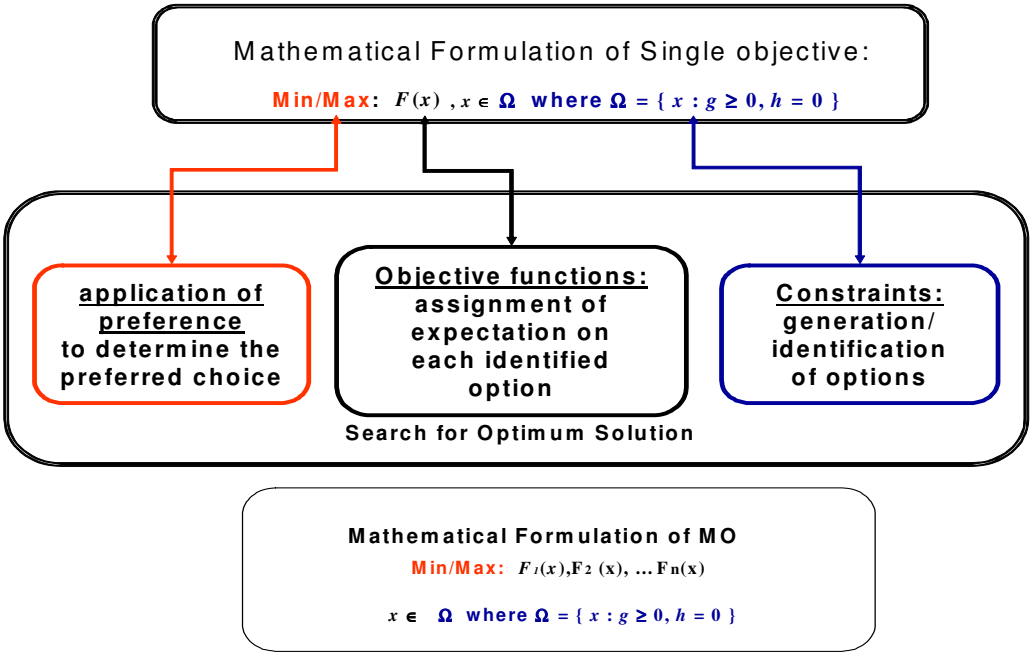


Figure 3-4. Illustration of common optimisation methodologies

3.3.2. Trade-offs in deciding the conflicting objectives

As already explained earlier, optimum design with refer to economic criteria might not be optimum design with refer to environmental criteria. Figure 3-5 outlines the relationship between total environmental cost and environmental impact. It is trade-off relationship where

decision making can be subjective options from stake holder and it is explained by 'the rule of expectations'. This indicates that decreasing total environmental impact from E2 to E1 has consequence increasing total cost from C2 to C1 and visa versa. In real application, for instance, reducing certain amount of industrial waste according to end-of-pipe treatment policy will be fulfilled by the additional of equipment purchase, changing of more friendly solvent, high temperature reaction to increase reaction rate hence reducing unreacted materials, etc.

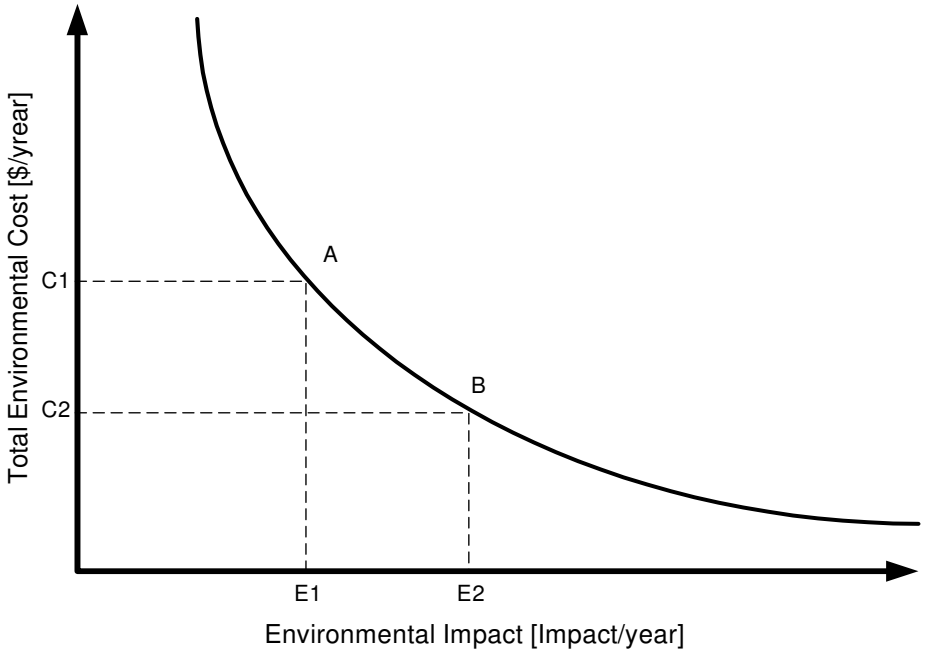


Figure 3-5. Trade-off between environmental impact and total environmental cost [72]

Also, in safety point of view, improving plant safety may lead to increasing capital cost. This cost is needed in order to equip the plant to fulfill certain level of safety. Figure 3-6 shows this relationship. As the safety level is intended to be improved (e.g. safer condition will be obtained), the consequence is decision maker must provide plant with the more reliable equipment, structure or design and consequently expenses are needed. In other hand, through this increasing safety level, the risk in the plant is expected to decrease. The total safety costs can be expressed as follows:

$$C_T = C_{SIM} + C_{IRR} \qquad (3\text{-}2)$$

Where C_T is total cost for safety, C_{SIM} is costs for investment in safety instrumentation and maintenance and C_{IRR} for insurance and residual risk costs. This relationship can be illustrated in the figure 3-6 below.

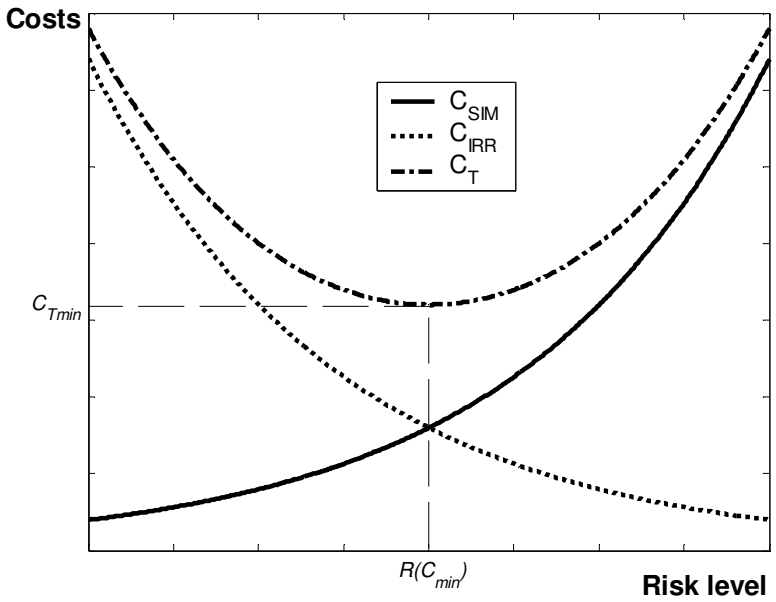


Figure 3-6. Illustrative relationship between safety cost and risk level. C_{SIM}, C_{IRR} and C_T represent safety investment and maintenance costs, insurance and residual risk costs and total safety costs respectively. C_{Tmin} and $R(C_{min})$ represent minimum total safety costs and risk level for minimum safety costs respectively [144]

From those both trade-off illustrations, there is a necessity to take into account trading-off methodology to compromise between environmental, safety and cost conflicting objectives which are conflicting each others. Through multiobjective optimisation, the trade-off will be considered to support a decision making policy regarding optimum environmental and safety purposes while satisfying plant profit.

3.3.3. Survey on advanced optimisation

Three advanced optimisation programs attracted many researchers to use recently in order to find the best solution. Those three optimisation programs are multiobjective optimisation, simulated annealing and genetic algorithm.

Application examples of simulated annealing and genetic algorithm have been described by Diwekar [43]. Also, the integration of simulated annealing to a simulation tool for dynamic optimisation of chemical processes has been performed by Li, Löwe, Garcia and Wozny [95]. Detail explanation of simulated annealing and genetic algorithm program will be beyond this thesis. Then, following section will explain multiobjective optimisation.

3.3.4. Multiobjective optimisation

The mathematical expression of multiobjective optimisation program can be formulated as follows [33]:

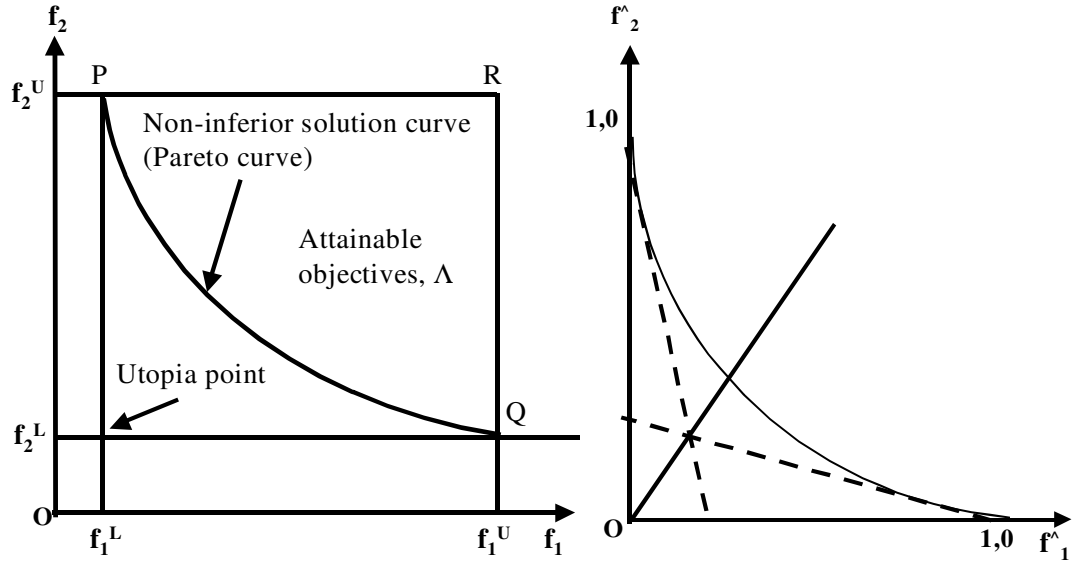
$$\min_{x\in\Omega} F(x) = \left[f_1(x), f_2(x), ..., f_n(x)\right]^T \qquad (3\text{-}3)$$

where n ≥ 2 and Ω (constraint set) = {x: h(x)=0,g(x) ≤ 0, a ≤x≤b}, which denotes the feasible set of equality constraints, h(x), inequality constraints, g(x), and explicit variable bounds, respectively. The space belongs to objective vector is called objective space or criterion space. Non-inferior solution of multiobjective optimisation program, or called as Pareto optimal, can be obtained if and only if there is no $x \in \Omega$, such that $f_i(x) \leq f_i(x^*)$ for all $i \in \{1,2,..,n\}$. Also, non-inferior has characteristic that there is no decrease within the set can be made in any of the objectives without causing a simultaneous increase in one or more of the objectives.

According to figure 3-7a, Pareto frontier is laid along PQ line to represent results generated by one objective function (f_1) with respect to another (f_2). The area under PQR is attainable objectives, Λ, which is defined as $\Lambda=\{ (f_1,f_2)$, where $x \in \Omega)\}$. The point (f_1^L, f_2^L) can be defined as the utopia point. This utopia point will generally not feasible because it will lie beyond attainable objectives. Therefore, following normalization, as shown in figure 3-7b, can be employed:

$$\hat{f}_1 = \frac{f_1 - f_1^L}{f_1^U - f_1^L}, \hat{f}_2 = \frac{f_2 - f_2^L}{f_2^U - f_2^L} \qquad (3\text{-}4)$$

where $\hat{f}_1$ and $\hat{f}_2$ represents the normalized objective functions, explicitly $0 \leq \hat{f}_1 \leq 1$ and $0 \leq \hat{f}_2 \leq 1$. In the normalized objective, utopia point lies at the origin, ***O***. With this normalized Pareto curve, one compromise point from many optima can be defined through the straight line created by crossing over the intersection point between two tangent lines of respective normalized objective functions, as shown in figure 3-7b.



a. Convex pareto curve

b. Normalized pareto curve

Figure 3-7. The concept of non-inferior solution curve (a) and its normalized curve [78], [79].

4. Decision Criteria

The role of the criteria evaluation in the decision making analysis is to map decisions of alternative design into quantitative indicators that enable the decision maker to access the degree to which various design alternatives advance the goals of design problems. This is done through criteria development.

While process model will represent design criteria into material flows and utility consumption required, criteria models represent physical information into measures of performance. More often there are tradeoffs, in which one criterion has higher desired objectives but lower desired objectives of another one, or vice a versa. In such cases it is necessary to summarize the vectors of criteria into measures of performance that can be used to rank alternatives. Accordingly, criteria development is necessary to rank alternatives and to give insights regarding the most promising design. Therefore, this chapter shall argue that the use of appropriate criteria is fundamental to enable decision makers to identify superior alternatives. This chapter is organized into the five major sections, namely fundamentals terms, economic criteria, environmental criteria, safety criteria and controllability criteria.

4.1. Fundamentals

4.1.1. Objective function

Mathematical modelling of basic evaluation comprises components such as streams, environmental impacts and costs vectors. The core of the evaluation procedure is finding an optimum solution with regard to particular objective function. If only one objective function is involved, the objective function is formulated as follows [126]:

$$f(S) = \min_{u}\left\{ c(u) + \sum_{i=1}^{n_P} f(P_i) \right\} \qquad (4\text{-}1)$$

where S is a given problem usually represented by a stream which must be processed (e.g. separated into its constituent components), u is the list of available alternatives, c(u) is the cost of a unit instance applied to the stream associated with problems S, and P_i, i=1,…,n_p is the sub problems generated from the outputs of the unit instance. The evaluation procedure can be extended into simultaneously generate multiple criteria. Then, the single objective function in equation 4-1 is replaced by a vector of m objective functions:

$$f(S) = \begin{bmatrix} \min_u op_1(c_1(u), \{f_1(P_i)\} \\ \min_u op_2(c_2(u), \{f_2(P_i)\} \\ \vdots \\ \min_u op_m(c_m(u), \{f_m(P_i)\} \end{bmatrix} \qquad (4\text{-}2)$$

with m corresponding criteria, each of which is minimised over a range of unit designs alternatives, u, and the set of subproblems P_i associated with the outputs of each unit design alternative. The costs returned both by unit design and the solutions to the subproblems are combined using a criterion specific operation, op_j. Each objective functions returns a list of N solutions ranked according to the particular criterion. Therefore, the solution list for a subproblem S consists of m lists with up to N entries each. The description of each criterion will be discussed in the next sections.

4.1.2. Type of criteria

Classification of design criteria is a specific task for the decision maker. According to Korevaar [93], classification may be:

1. Knock out criteria. These criteria are formulated as a structure, with the possible answer yes or no so that the criteria are be able to distinguish very fast among the alternatives, without going into much detail. The criteria then acts as a very rough filter.
2. Normative criteria. These criteria are formulated as a question which have a spectrum of answer such as weak/medium/strong or high/medium/low so that the results can be weighted and the trade-off or compromise solution can be made.
3. Reference criteria. These criteria are formulated as an equation with relative number of an answer so that the results can represent a measure of improvement or worsening achieved by alternative selection. For instance, the total amount of raw materials used per unit product or economic expensed per unit production of a base case.

The decision maker will determine the criteria for the design and afterwards the final decision is valuated against the criteria from problem definition step. The purpose of the criteria satisfaction is to investigate whether a design fulfills the design objectives.

4.1.3. Weighting factor

In multicriteria decision making, weighting factor reflects the relative importance of one criterion to other criteria under consideration. The weight value is not only dependent on the importance of any criterion, but also dependent on the possible range of the criterion values.

For the application in economic and environmental decision making, for instance, Schultz [118] explained some ecobalance weighting factors, as tabulated in table 4-1 below. The weighting factors can be applied for different fields of application such as sustainable development assessment, decision making in national or regional politics and environmental policy decision making in European society-base applications. The values in the weighting factors are defined according to a ranking of impacts into the desired objectives. According to Mallick, Cabezas, Bare and Sikdar [107], the weighting factors consider eight impact categories. From the table 4-1 shows that, for the application in sustainable development field, the global warming potential category places the most important consideration. Next, it is followed by the ozone depletion potential and energy factor categories as the second and the third important consideration.

Table 4-1. Weighting factors for the evaluation of environmental criteria [118].

Impact categories	Weighting factors			
	Sustainable development	**Political objective (long term)**	**Political objective (short term)**	**Europe society/ Europe barometer**
Global warming potential	28%	20%	9%	16%
Ozone depletion potential	22%	24%	43%	18%
Acidification potential	6%	18%	18%	15%
Euthropication potential	6%	16%	9%	16%
Ecotoxicity potential	16%	8%	5%	11%
Energy factor	17%	7%	4%	13%
Resource factor	1%	1%	1%	1%
Waste quantity of waste	4%	6%	11%	10%
Sum	**100%**	**100%**	**100%**	**100%**

4.1.4. Decision ranking

Ranking will be arranged based on qualitative or quantitative criteria evaluations. The evaluation outcome then will give scores or values that can be collected in a decision ranking comprising a set of columns or rows. The decision ranking tool will allow decision makers to structure and solve their problems by [93]:

1. specifying and prioritizing their needs with a list of criteria
2. then evaluating, rating and comparing the different solutions
3. and finally selecting the best alternatives

A decision alternative x is evaluated on each criteria, i, by means of a valued of function $v_i(x)$. Under the assumption of mutual preferential independence of criteria, decision maker can evaluate the overall value of an alternative x as [68]:

$$v(x) = \sum_{i=1}^{n} w_i \cdot v_i(x) \qquad (4\text{-}3)$$

where n is the number of criteria, w_i is the weight of criteria i, and $v_i(x)$ is the rating of an alternative x with respect to criteria i. The sum of the weights is normalized to one, and the component value functions $v(x)$ have valued between 0 and 1. The weights w_i indicate the relative importance of criteria i changing from its worst level to its best level, compared with the changes in the other criteria.

4.1.5. Analytical Hierarchy Process (AHP)

One method to solve multicriteria decision making problems is the analytical hierarchy process (AHP) methodology. The AHP methodology formulates multicriteria decision into a hierarchical structure of definite criteria, assess the relative importance of these criteria, compute alternatives for each criterion and determine an overall ranking of the alternatives[115].

According to Saaty [115], the Analytical Hierarchy Process is a decision approach designed to aid in the solution of complex multiple criteria problems in a number of application domains. This method has been found to be an effective and practical approach that can consider complex and unstructured decisions.

In analytical hierarchical process (AHP), the decision maker defines value or score for each alternative using pairwise comparison technique. This pairwise comparison technique compares two alternatives (that is a pair) according to definite criteria and indicating a preference. For example, design A will be compared to design B to decide which design is the most preferred according to some criteria (e.g., economy, environment, safety, etc.). The comparison will be performed using preference scale that gives numerical value for preference ranking.

The standard for AHP values is tabulated in table 4-2. This scale has been determined and well recognised for decision making using AHP method as an appropriate tool for comparing two alternatives. For example, if design A is moderately preferred compared to design B, then this comparison will be given a value of 3. The value of 3 in this preference ranking is a measure from preference from decision of one alternative compared to another alternative.

Table 4-2. Pairwise comparison scale

Preference or verbal judgment	Value
Extremely preferred	9
Very strong to extremely preferred	8
Very strongly preferred	7
Strongly to very strongly preferred	6
Strongly preferred	5
Moderately to strongly preferred	4
Moderately preferred	3
Equally to moderately preferred	2
Equally preferred	1

The selection of the methodology is based on the characteristics of the inherent problem and the consideration of the advantages and drawbacks of other methodologies. The decision-maker judges the importance of each criterion in pair-wise comparisons. The outcome of AHP is a prioritised ranking or weighting of each decision alternative. Basically, there are three steps for considering decision problems by AHP: constructing hierarchies; comparative judgement; and synthesis of priorities, described as follows.

Constructing hierarchies

This step allows a complex decision to be structured into a hierarchy descending from an overall objective to various 'criteria', 'sub-criteria', and so on until the lowest level. The objective or the overall goal of the decision is represented at the top level of the hierarchy. The criteria and sub-criteria contributing to the decision are represented at the intermediate levels. Finally, the decision alternatives or selection choices are laid down at the last level of the hierarchy. According to Saaty [115], a hierarchy can be constructed by creative thinking, recollection and using people's perspectives.

Comparative judgements

Once the hierarchy has been structured, the next step is to determine the priorities of elements at each level (*'element'* here means every member of the hierarchy). A set of comparison matrices of all elements in a level of the hierarchy with respect to an element of the immediately higher level are constructed so as to prioritise and convert individual comparative judgements into ratio scale measurements. The preferences are quantified by using a nine-point scale. The meaning of each scale measurement is explained in table 4-2. The pair-wise comparisons are given in terms of how much element A is more important than element B.

4.2. Economic Criteria

Since a principal objective for developing a chemical process is to gain profit, then the typical objective in use has monetary units. Within the process model, the design criteria can transform flow rates (energy and mass flowrates) and process equipment specifications and yield the information of revenue and cost information, as tabulated in the table 4-3 below.

Table 4-3. Economic information from the process model

Process/equipment model	Price/ Cost
Mass flowrates of product ($\dot{m}_p$), mass balance	Revenue
Mass flowrates of raw materials ($\dot{m}_{raw}$), mass balance	Raw material costs (P_{raw})
Mass flowrates of by products and wastes ($\dot{m}_w$), mass balance	Waste treatment and disposal costs (P_w)
Energy consumption rate ($\dot{Q}$), energy balance	Energy or utility costs (P_e)
Dimension of major equipment, model equation of unit	Capital cost (C_{capt})

For comparison of design alternatives, the term of economic potential (EP) is used [45]. The higher economic potential is the more promising the design alternative. From the table above, the first two sets of information can be transformed into economic potentials calculation as follow:

$$EP_1 = Revenue - raw\ material\ costs$$
$$= \sum \dot{m}_p \cdot P_p - \sum \dot{m}_{raw} \cdot P_{raw} \quad (4\text{-}4)$$

Then, the difference between the above economic potential and the costs accounted from the third and fourth row of table above yield the ultimate economic profit:

$$EP_2 = EP_1 - Waste\ treatment\ and\ disposal\ costs - energy\ costs$$
$$= EP_1 - \sum \dot{m}_w \cdot C_w - \sum \dot{Q} \cdot C_e \quad (4\text{-}5)$$

where $\dot{m}$ represents flowrates of products or byproducts/waste in $\frac{kg}{year}$ and P represents prices in $\frac{€}{year}$.

The conversion of equipment sizes into capital cost typically takes place according to the information summarized in the following table 4-4.

Table 4-4. Basic of the economic potential calculation

Variable costs	Sources of calculation
Purchase equipment costs (C_{PE})	Equipment cost correlation
Total installed equipment cost or total module cost	C_{PE} is multiplied by a series of factors and account for: • Direct material and labour used for installation • Indirect installation • Contingencies and fees
Fixed capital investment (C_{FCI})	Additional factors to account for necessary investments in auxiliary facilities (e.g. utility and waste treatment plant)

The costs of specific item of equipment will be a function of function of:

- Size
- Materials and construction
- Design pressure
- Design temperature

Cost data are often presented as cost versus capacity charts, or expressed as a power law of capacity:

$$C_E = C_B \cdot \left(\frac{K}{K_B} \right)^M \quad (4\text{-}6)$$

where

- C_E : equipment cost with capacity K,
- C_B : known base cost for equipment with capacity K_B
- M : constant depending equipment type.

To update the costs data available from the literature, one can use cost indices:

$$\frac{C_1}{C_2} = \frac{Index_1}{Index_2} \qquad (4\text{-}7)$$

where :

- C_1 = cost of equipment in year 1
- C_2 = cost of equipment in year 2
- $Index_1$= cost index in year 1
- Index $_2$= cost index in year 2

The sources of cost index can be found from:

- Chemical engineering index
- Marshal and swift index
- Nelson – farrar cost index

Apart from the purchased cost of equipment, calculation of installation costs requires data costs for:

- Cost of installation
- Piping and valves
- Control systems
- Foundations
- Structures
- Insulation costs
- Fire proofing
- Electrical costs
- Painting costs
- Engineering fees
- Contingency

In addition, according to Douglas [45], the Guthrie's correlation can be used for equipment cost calculation:

1. For cost calculation of distillation tower (without column internal):

$$C_{DT} = \left[\frac{M\ \&\ S}{280}\right] \cdot (101.9) \cdot D^{1.06} \cdot H^{0.862} \cdot (2.18 + F_c) \qquad (4\text{-}8)$$

where *M&S* is the Marshal and Swift index, *D* is column diameter, *H* is column height and *Fc* corresponds to the correction factor for material, pressure, etc.

2. For cost calculation of heat exchanger cost:

$$C_{HE} = \left[\frac{M\ \&\ S}{280}\right] \cdot (101.3) \cdot A^{0.65} \cdot (2.29 + F_c) \qquad (4\text{-}9)$$

where A is the heat transfer area of a heat exchanger in m^2.

From table 4-4, the capital cost can be calculated which covers approximately major equipment costs or 20 – 40% fixed capital investment, C_{TM} [45]. Then, the annualized cost is calculated via the annualization factors, *AF,* according to following equation:

$$\text{AC} = AF \cdot C_{TM} \qquad (4\text{-}10)$$

where *AC, AF* and C_{TM} represent annualized costs, annualized factor and investment cost, respectively. The value of annualization factor can use following standards in the table 4-5 below:

Table 4-5. The calculation method for annualization factor

References	**AF calculation**
Smith [122]	$AF = \frac{i \cdot (1+i)^N}{(1+i)^N - 1}$ (4-11) Where: i : the applicable annual discount rate N: the number of years over which the capital cost is annualized
Ulrich [138]	$0.15 \leq AF \leq 0.20$ (4-12)
Douglas [45]	$AF = 0.191 + (2.42 \cdot CCF)$ (4-13) Where: CCF : capital cost factor that equals to following equation below: $CCF = \frac{\left[\frac{1}{n}\left[(1+i)^n - 1\right] + 0.295 \cdot i - \frac{\tau}{N}\right] \cdot (1+i)^N - 0.225 \cdot i - \frac{\tau}{N}}{1.3 \cdot (1-\tau) \cdot \left[(1+i)^N - 1\right]}$ (4-14) Where: n : length of period of construction (year) N : number of years of operation i : discount rate τ : tax rate

Illustrative examples for applying the annualization factor, can given according to Smith [122] and Douglas [45] below:

Smith´s calculation
For instance, if the value of i=15% and the value of N=11 years, then the annualization factor shall be 0.191 y^{-1}
Douglas´s calculation
For example, if the value of i = 15%; n= 4 years; N=11 years; τ =48%, then the value of CCF= 0.358 y^{-1} and hence AF = 1.06 y^{-1}.

When including the annualized costs economic at the conceptual design stage, the economic objective function to be considered becomes:

$$EP3 = EP2 - AC = EP2 - (AF \cdot C_{TM}) \quad (4\text{-}15)$$

And, if the economic calculation takes into consideration the economic margin, the variable costs should be included. The economic margin follows the equation:

$$Economic\ margin = Revenue - Variable\ costs \quad (4\text{-}16)$$

The variable costs consider all direct and indirect economic variables (e.g: labor costs, depreciation, etc). However, for integration of such costs calculation will become too difficult using the mass and economic balances from process simulators.

If plant management requires an improvement of their plant, then an improvement projects will be scheduled and the costs associated with the improvement projects must be calculated. The improvement in performance sought is often an increase in the throughput. However, estimating the capital cost of an improvement project is much more difficult than for new design [123]. Therefore, the costs factors of modifications projects are resumed in order to handle the absence of cost data information. For improvement projects, the basis for capital costs calculation is started with the required investment in the new equipments.

If old equipment needs to be modified to take up new role, then the installation cost must be applied without the equipment cost. It means, in absence of information, the designer or decision maker should take the equivalent piece of new equipment. Since all improvement projects have individual characteristics then the analysis of the costs must come into detail. In absence of such detail cost data, a very preliminary estimate can be obtained by estimating the retrofit costs for a new design but without equipment costs [123]. For example, the cost factor of modification project for distillation column is tabulated below [123]:

Table 4-6. Cost factors for distillation column modification [123].

Column modification	Cost factors of modification (multiply factor by cost of new equipment)
Removal of trays to install new trays	0.1 for the same tray spacing 0.2 for different tray spacing
Removal of trays to install packing	0.1
Removal of packing to install new trays	0.07
Installation of new trays	1.0 – 1.4 for the same tray spacing 1.2 – 1.5 for different tray spacing 1.3 – 1.6 when replacing packing
Installation of new structured packing	0.5 – 0.8

For estimation of the purchase cost of new structured packing the formula and data of C_B and M can be found in Smith's book [122]. For purchasing a 5-m height of new structured packing with a diameter of 0.5 m the purchase cost of this packing with that specification is 1.8×10^4 \$ and the value of cost exponent (M) is 1.7.

As illustrative example, for instance, a company management intends to revamp and increase capacity of an existing distillation column by replacing the existing sieve trays with stainless steel structured packing. The column shell is 46 m tall and 1.5 m diameter and currently fitted with 70 sieve trays with a spacing 0.61 m. The existing trays are to be replaced with stainless steel structured packing with a total height of 30 m. Here, the task of this improvement project is estimating the cost of an improvement of an existing distillation column. It gives the purchase cost as:

$$C_{E,packing} = C_B \cdot \frac{H_1}{H_2} \cdot \left(\frac{D_1}{D_2}\right)^M = 1.8 \cdot 10^4 \cdot \frac{30}{5} \cdot \left(\frac{1.5}{0.5}\right)^{1.7} = 6.99 \cdot 10^5 \$$$

Adjusting to the cost to bring up it up-to-date using the ratio of cost indexes (equation 4-7):

$$C_{E,packing\,(adjusted-in-time)} = C_{E,packing} \cdot \left(\frac{I_1}{I_2}\right) = 6.99 \cdot 10^5 \cdot \left(\frac{441.9}{435.8}\right) = 7.09 \cdot 10^5 \$$$

From table 4-6, the factor for removing the existing tray is 0.1 and that for installing the new packing is 0.5 to 0.8 (say, 0.7). Therefore, the estimated total cost of the project:

$$C_{Modification} = (1 + 0.1 + 0.7) \cdot 7.09 \cdot 10^{-5} = 1.28 \cdot 10^{6} \$$$

4.3. Environmental criteria

Historically, system optimisation in chemical and process engineering applications has focused on maximising the economic performance, subject to the certain constraints in the system. With increasing awareness for cleaner environment over the past decade, optimisation of environmental performance has started to be incorporated into system optimisation, alongside traditional economic criteria. These approaches have mainly been focused on various waste minimisation techniques, such as process intensification and integration [[49], [50] as well as pollution reduction methodology [107].

The attempts to incorporate environmental considerations into the design and optimisation procedures represent the beginning of the paradigm shift in the process industry which traditionally oriented towards the economic performance of the process. Such attempts to introduce environmental aspects in chemical processes design are called environmental conscious process design (ECPD) [5]. The objective of ECPD is to generate environmentally sustainable and economically feasible chemical process. Intensive works in ECPD field are overviewed in the table 4-7 below.

Table 4-7. Selected references for environmental conscious process design.

References	Description
Alexander, Barton, Pitrie, Romagnoli [4]	Developed a structural methodology for environmental design in process synthesis and optimisation.
Bakshi [12]	Proposed a thermodynamic framework for ecologically conscious process design. Described the application of exergy and emergy as indicators for assessing chemical system. The new term of "emergy " is defined as the total solar equivalent available energy of one from that was used up directly and indirectly in the work of making a product or service.
Biwer, Heinzle [19]	Proposed an environmental assessment method in chemical process in early stage of process development. Proposed a qualitative method for environmental impact assessment based on 'ABC' criteria.
Burgess, Brennan [24]	Explained the application of life cycle assessment for optimisation in chemical processes.
Chen, Shonnard [32]	Developed a systematic methodology for environmental conscious chemical process design. Some environmental impacts as well as economic indicators were proposed for optimisation procedure.

Table …Selected references for environmental conscious process design (*continued*)

Douglas [44]	Proposed a hierarchical procedure for process synthesis for waste minimisation purposes.
Jin, Wang, Wei [77]	Described a basic understanding on ecological perspective in chemical engineering.
Krajnc, Glavic [90]	Explained some indicators in chemical process manufacture towards sustainable production in chemical processes.
Koller, Fischer, Hungerbühler [91]	Introduced a methodology to assess safety, health, and environmental impact simultaneously in early process development.
Mallick, Cabezas, Bare, Sikdar [107]	Proposed the application of waste reduction algorithm (WAR) to reduce pollution in chemical processes using process simulators.
Smith [122]	Evaluation the economics and environmental friendliness of conceptual designs for new and retrofitted chemical processes.

4.3.1. Basic requirements in environmentally conscious process design

For the purposes of decision support methodology in environmentally conscious process design, three requirements are needed, namely technology base, data base and assessment methodology, as shown in the figure 4-1 below.

In technology base aspect, first of all, particular real chemical process is defined. Then, to prepare for thorough assessment, a process model is developed. With the aid of process simulators available recently, a process model is developed to structurally represent the real chemical processes under investigation.

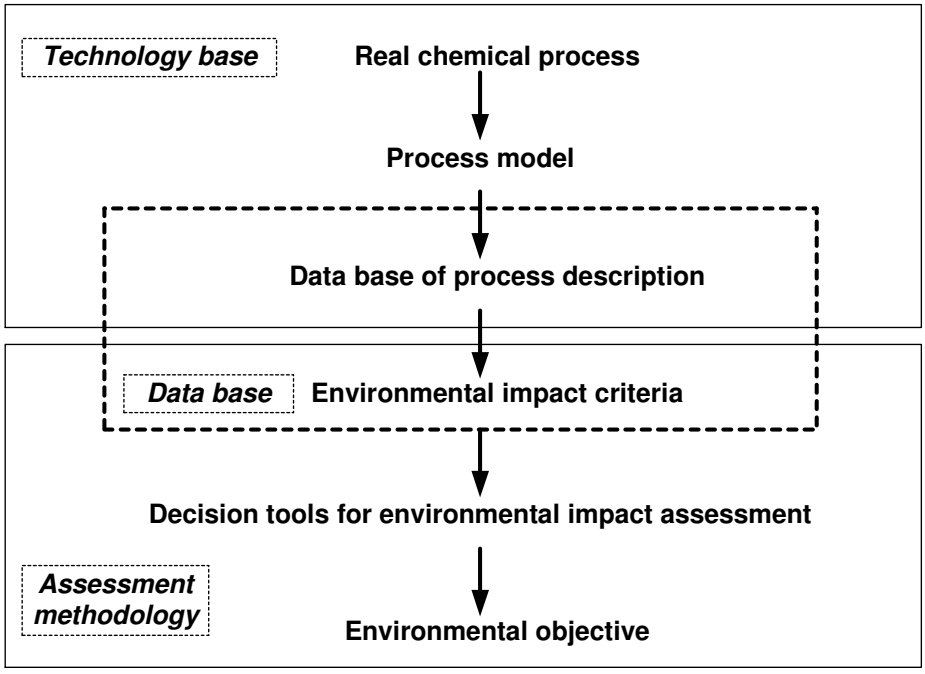


Figure 4-1. Basic requirements for running decision support methodology in ECPD

Next, a data base containing the process description and environmental impact criteria are fulfilled. Process description consists of data regarding dimension, operating condition

and raw materials employed, whereas environmental impact criteria consists of limit values regarding measurable impact associated with operating condition as well as individual raw materials employed for chemical manufacturing.

At the end, assessment methodology must be defined in order to assess environmental performance of the process under investigation. In this assessment methodology, the decision tools are used in order to meet ultimate environmental objective, which is minimising the impacts of process into environment.

4.3.2. Designing scope and target

According to Hoffmann, Hungerbühler and McRae [72], at the beginning of the design process, the scope of the study should be defined and key assumptions should be stated. A major decision concerns the definition of the relevant balance region and the identification of constraints such as site-specific factors. As advocated earlier, the balance region should, in principle, comprise the process itself, the production of raw materials and utilities, and the treatment of waste streams. This approach takes into account of all environmental effects related to the production of the desired chemical. Figure 4-2 shows the balance region for defining the scope to improve environmental performance of chemical processes.

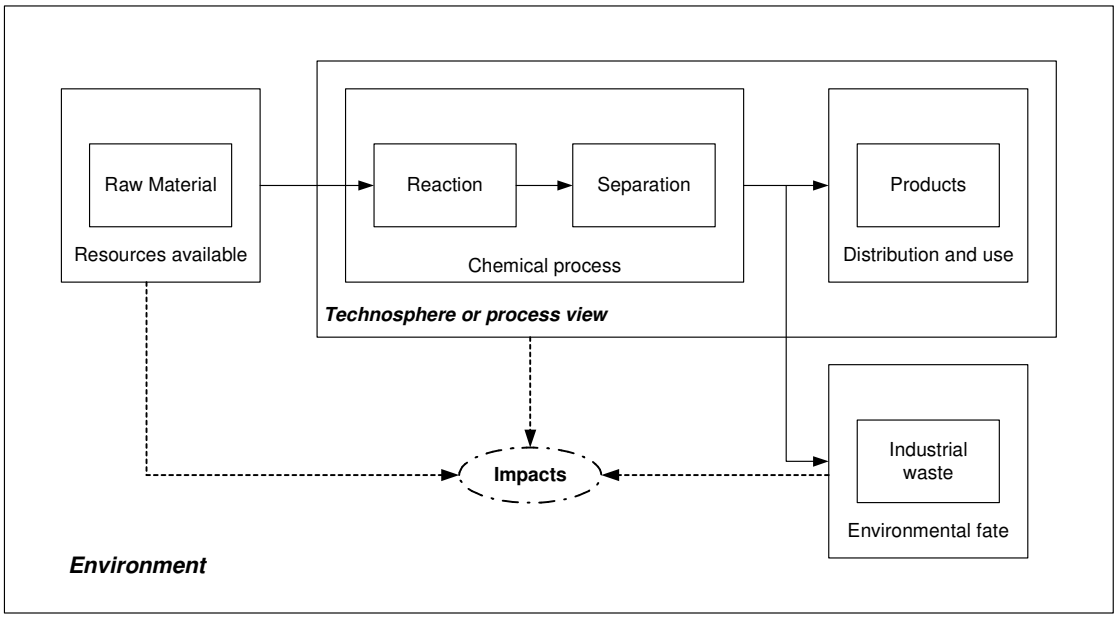


Figure 4-2. Scope of decision space for assessing environmentally conscious process design [72].

In implementing the environmental impact assessment, the impact scales are distinguished according to the area that can be affected by the impacts, either influence global, national or local scale/ area. Further, the environmental impact indicators are classified based on the influence on ecological system, resources availability and health risk associated with environmental problems. The illustration of matrix relationship between environmental indicators and the area affected is depicted in figure 4-3 below. The environmental impact metrics commonly used for the valuation of environmental indicators are tabulated in the table 4-8 below.

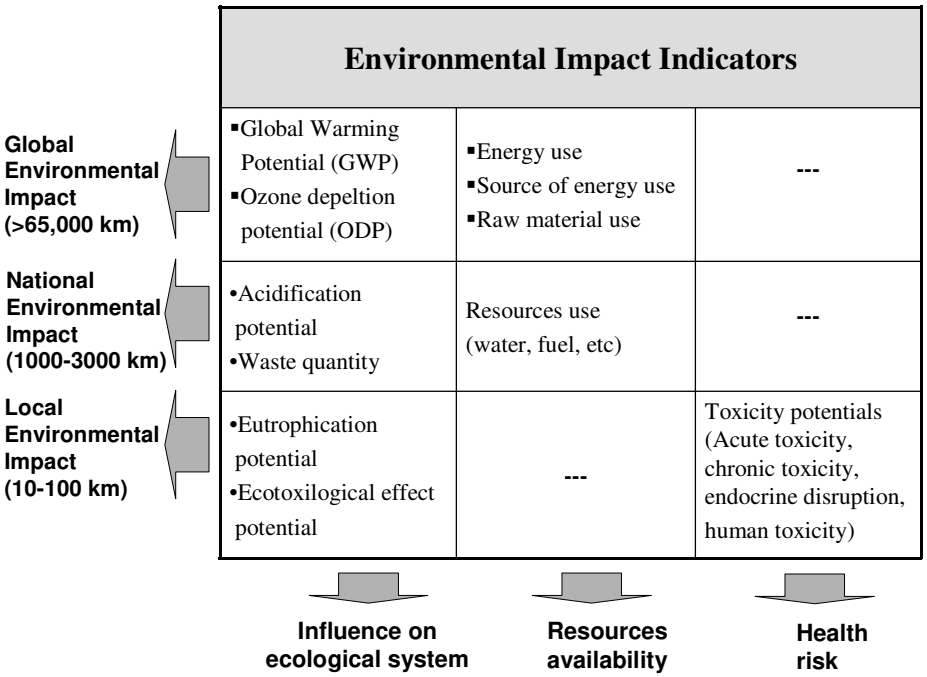


Figure 4-3. Classification of environmental impact indicators [adapted from [62], [116].

Table 4-8. Commonly used environmental impact metrics [5],

Environmental problems	Impact indicators used	Example of substances	Relevance
Climate change	Global warming potential (GWP)	CH_4	The GWP is expressed as kg of CO_2 equivalents per kg of substance.
Stratospheric ozone depletion	Ozone depletion potential (ODP)	HCFC – 141b	The ODP is expressed as kg of CFC-11 equivalents per kg of substance
Photochemical smog	Photochemical oxidants creation potential (POCP)	Ethanol	The POCP is expressed as kg of ethylene equivalents per kg of substance
Acid deposition	Acidification potential (AP)	PM_{10}	The AP is expressed as kg of SO_2 equivalent per kg of substance

4.3.3. Valuation of environmental impact

The objective of environmental impact factor (EIF) is to compromise the best decision for minimising waste while satisfying economic objectives. The decision of best process design is very useful mainly for early design stage of chemical process development. For decision making at the early and operating stages, the assessment tool directed to environmental protection should be simple and reliable to represent or predict future improvement

possibilities. Following sections discuss two valuation models of environmental impact for chemical processes, namely waste reduction algorithm model and ABC models.

4.3.3.1. Waste reduction algorithm (WAR) methodology

Waste reduction algorithm (WAR) [107] focuses on a relative effect from certain process modification that calculated through potential environmental impact (PEI) for particular product. This PEI represents relative measure for chemicals to have an adverse effect to human health and environment and evaluated from some pollution indices. The PEI is a conceptual quantity that cannot be measured. However, it can be calculated from related measurable quantities.

In the WAR algorithm, a quantity called as 'Pollution Index' is defined to measure the waste generation in a process. This index also allows comparison of pollution production of different processes. Logical flow of the waste reduction algorithm is explained in the appendix. Impact indicators are compiled according to their relative measurements as tabulated in the table 4-9 below. The complete example and application of each indicators can has been described by Allen and Shonnard [5] in the Appendix D of their book.

Table 4-9. Impact indicators according to relative measurement of ambient environment and toxicity [5]

Type of indicators	Relative Risk Index	Equation
Indictors of ambient environment	Global warming	$\dot{I}_{GW,i} = N_C \frac{MW_{CO_2}}{MW_i}$
	Ozone depletion	$\dot{I}_{OD,i} = ODP_i$
	Smog formation	$\dot{I}_{SF,i} = \frac{MIR_i}{MIR_{ROG}}$
	Acid rain	$\dot{I}_{AR,i} = \frac{ARP_i}{ARP_{SO_2}}$
Indicators of toxicity	Human toxicity ingestion route	$\dot{I}_{ING} = \frac{C_{W,i} \cdot LD_{50,toluene}}{C_{W,toluene} \cdot LD_{50,i}}$
	Human toxicity inhalation route	$\dot{I}_{INH} = \frac{C_{A,i} \cdot LC_{50,toluene}}{C_{A,toluene} \cdot LC_{50,i}}$
	Human carcinogenicity ingestion route	$\dot{I}_{CING} = \frac{C_{w,i} \cdot HV_i}{C_{w,benzene} \cdot HV_{benzene}}$
	Human carcinogenicity inhalation route	$\dot{I}_{CINH} = \frac{C_{A,i} \cdot HV_i}{C_{A,benzene}.HV_{benzene}}$
	Fish toxicity	$\dot{I}_{FT} = \frac{C_{W,i} \cdot LC_{50f,PCP}}{C_{W,PCP} \cdot LC_{50f,i}}$

The WAR algorithm itself is based on the generic pollution balance of a process flow diagram as given in equation below [107]:

Pollution accumulation = Pollution inputs + Pollution generation – pollution output (4-17)

The pollution balance equation is applied to the conservation of potential environmental impact in a process. The flow of impact in and out of the process is related to mass and energy flows but is not equivalent to them. The conservation equation can be written as:

$$\frac{dI_{sys}}{dt} = \dot{I}_{in} - \dot{I}_{out} + \dot{I}_{gen} \qquad (4\text{-}18)$$

If the considered impacts are from mass and energy flowrate, then the equations can be arranged as:

$$\frac{dI_{sys}}{dt} = \left(\dot{I}_{in}^{mass} + \dot{I}_{in}^{energy} \right) - \left(\dot{I}_{out}^{mass} + \dot{I}_{out}^{energy} \right) + \dot{I}_{gen} \qquad (4\text{-}19)$$

Where $\dot{I}_{sys}$ is the potential environmental impact content inside the process, $\dot{I}_{in}$ is the input rate of impact, $\dot{I}_{out}$ is the output rate of impact and $\dot{I}_{gen}$ is the rate of impact generation inside the process by chemical reactions or other means.

If the process is operated at steady state, then the potential impact of the system is constant over the time, and equation can be simplified to:

$$\dot{I}_{gen} = \dot{I}_{out} - \dot{I}_{in} \qquad (4\text{-}20)$$

which allows the calculation of the generated potential impact from the indices for streams entering and leaving the process.

A combined single value of impacts is used to evaluate environmental friendliness or unfriendliness of a given system and is defined as:

$$\dot{I}_{total} = \sum_{j=1}^{NI} w_j \cdot \dot{I}_j \qquad (4\text{-}21)$$

where *NI* is number of impact categories considered in the investigated system and w_j is weighting factor of impact category j.

The weighting factor represents relative or site-specific importance of the impact category. For instance, if the decision maker were evaluating a process that is located in an urban area having frequent smog alerts, the weighting factor for smog formation (i.e., POCP) would probably receive a high value. If total environmental impact of process (or

system) $\dot{I}_{total}$, A is lower than that of process B, then process A would be claimed as an environmentally friendlier process than process B.

As an illustrative example of WAR application, the hydrodealkilation of toluene (HDA) to make benzene is used, as has been already used by Smith [124]. Such flowsheet is shown in the figure 4-4 below, where toluene and hydrogen (with 5.0 mol% methane purity) are reacted to form benzene plus byproducts methane, biphenyl and hydrogen according to the reactions:

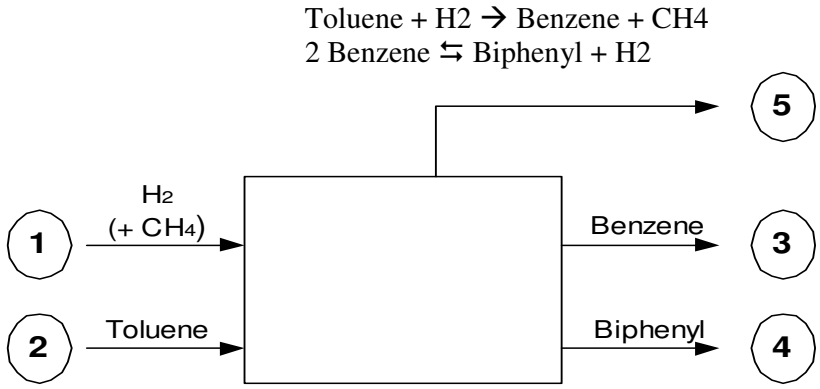


Figure 4-4. Process flow diagram of hydrodealkilation of toulene (HDA) to make benzene

Two simple alternative designs for the hydrodealkilation process are to consider reactor per pass conversion of toluene of 0.40 and 0.80. Unreacted toluene is recycled back to the reactor system in each case to obtain complete overall conversion. Considering this flowsheet, it is possible to do environmental evaluations. To start evaluations, WAR graphical user interface (WAR GUI) was used to generate potential environmental impact scores for the HAD process. Table 4-10 shows the environmental impact scores per kilogram for each impact category. Only certain impact categories were included, and that others could consider different categories to be important (e.g. resource depletion). From this table, it is obvious that hydrogen is not an environmental problem, methane is the only component with a direct effect on global warming, and none of these components have identified effects on acidification or ozone depletion.

Table 4-10. Potential environmental impact scores for components of the HDA process

$\psi_{i,j}$ (PEI/kg)	H2	CH4	Benzene	Toluene	Biphenyl
HTPI	0	0	0.1182	0.0.781	0.1191
HTPE	0	0	0.0923	0.0004	0.2953
ATP	0	0.057	0.0898	0.0645	0.8841
TTP	0	0	0.1182	0.0781	0.1191
PCOP	0	0.0144	0.3884	1.1569	0
AP	0	0	0	0	0
ODP	0	0	0	0	0
GWP	0	0.0035	0	0	0

The mass flowrates are multiplied by the scores of table 4-10 to create tables 4-11 and 4-12 with the weighting factors are assumed equal 1. Table 4-11 presents the five streams of figure 1 according to impact categories.

Results in the table 4-11 and 4-12 below are shown only for a reactor per pass conversion of 0.8. For a PEI generation calculation, streams entering a process have a negative impact values (see equation 4-19).

Table 4-11. Potential environmental impacts generated for streams of the HAD process according to impact categories

$\psi_{i,j}$ (PEI/kg)	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5
HTPI	0	-16,740	20,552	923	0
HTPE	0	-84	16,045	2,288	0
ATP	-123	-13,824	15,622	6,851	2,249
TTP	0	-16,740	20,552	923	0
PCOP	-31	-249,974	67,528	0	568
AP	0	0	0	0	0
ODP	0	0	0	0	0
GWP	-8	0	0	0	138
Total by stream		-295,363	140,229	10,985	2,955

Table 4-12. Potential environmental impacts generated by components of the HAD process according to impact categories

$\psi_{i,j}$ (PEI/kg)	H2	CH4	Benzene	Toluene	Biphenyl
HTPI	0	0	20,552	16,740	923
HTPE	0	0	16,045	-84	2,288
ATP	0	2.216	15,622	-13,824	6,851
TTP	0	0	20,552	-16,740	923
PCOP	0	537	67,528	-247,974	0
AP	0	0	0	0	0
ODP	0	0	0	0	0
GWP	0	130	0	0	0
Total by component	0	2,793	140,229	-295,362	10,985

According to Smith's design [124] between conversion of 0.40 and 0.80, there is a relatively small difference in economic potential. Then, the environmental criterion can be valuable criteria to decide the best design between these two design alternatives. Figure 4-5 shows the generation of potential environmental impact (PEI) for the several of impact categories. It is obvious from this figure that the PEI values for HTPE and ATP increase at the higher conversion while PCOP offsets these with a lower PEI value at the higher conversion.

The potential environmental impacts by stream presented in the table 4-11 are graphed in figure 4-6. Here one can see on which streams to take into consideration in order to improve environmental performance of the investigated process. The results indicate that streams 2 and 3 have the largest absolute magnitude, but one could consider that if only waste stream are important that stream 4 is greater in size than stream 5, with a relatively large change in stream 4 for the two conversions.

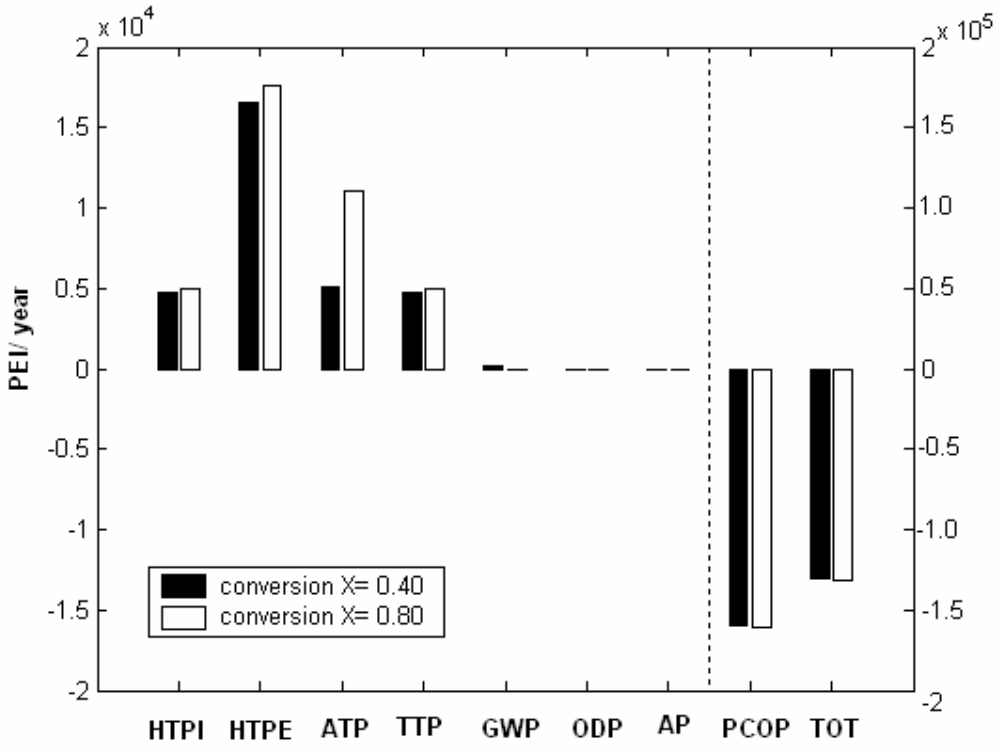


Figure 4-5. Potential environmental impacts generated by HDA process according to various impact categories (Bars to the right of the dotted line use the right axes labels)

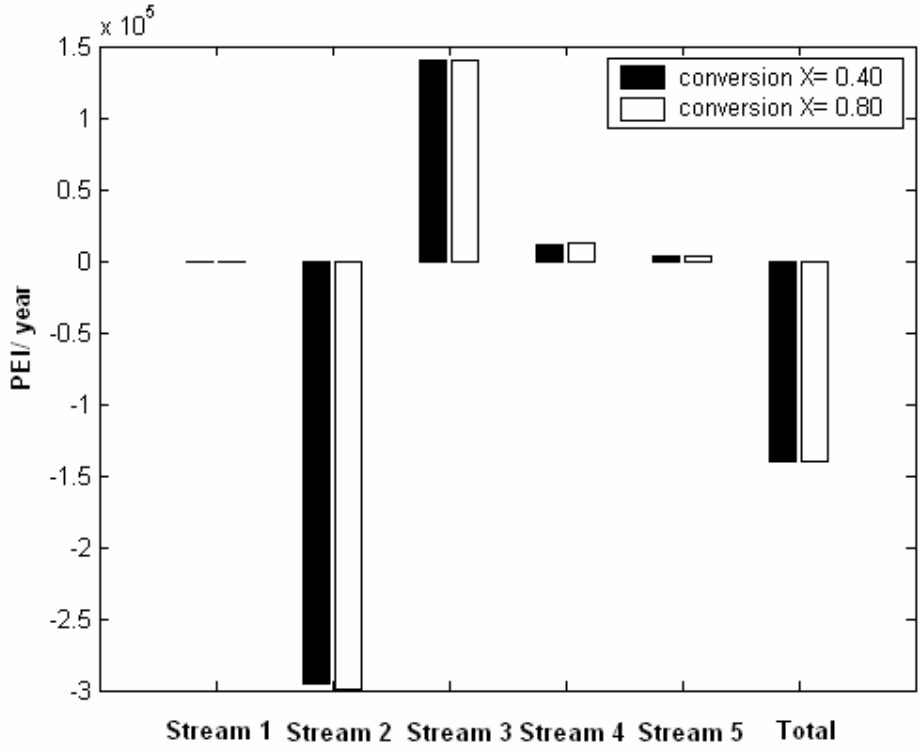


Figure 4-6. Potential environmental impacts generated by the HDA process according the process streams

Figure 4-7 shows the PEI by component. From the figure 4-7, it is obvious that the impacts of methane are determined by the two streams and toluene has a large effect on the total PEI by the process.

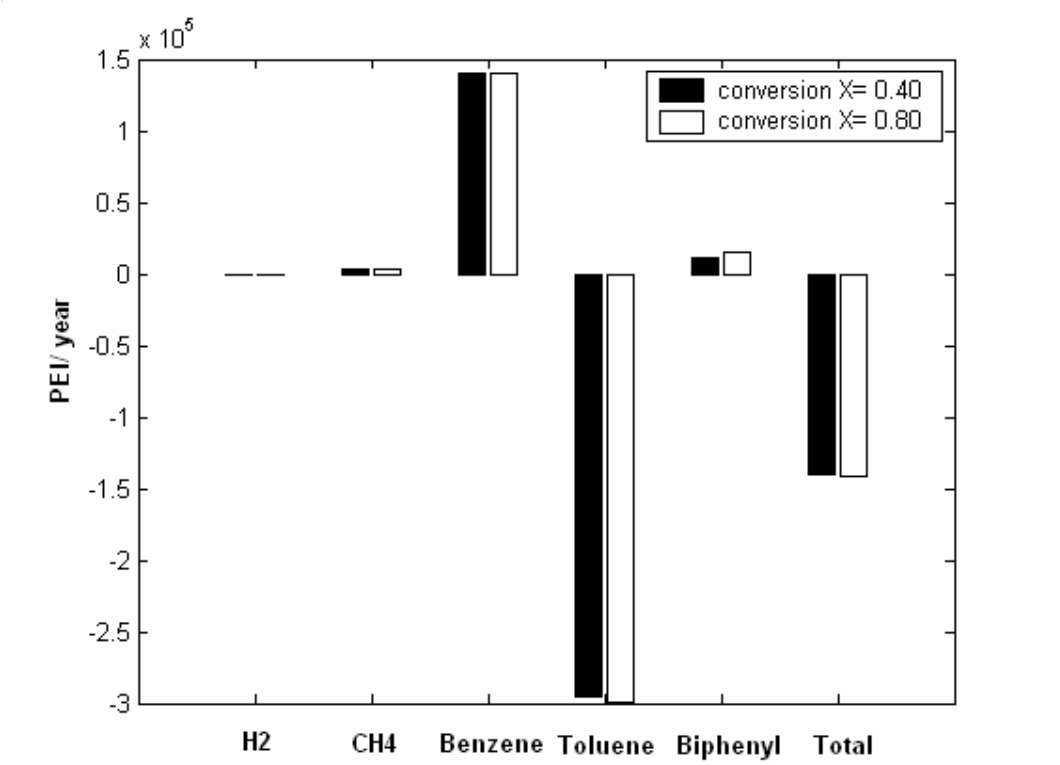


Figure 4-7. Potential environmental impacts by the HDA components

4.3.3.2. ABC methodology

The extension of environmental impact indicator was created by Heinzle and Hungerbühler [65], [66], [67] by allocating all mass streams to defined origins: coupled products associated with desired reaction, incomplete conversion, bad selectivity, impurities contained in substances, solvents, catalyst and other auxiliary materials needed. A more detailed environmental, safety and health and safety assessment of chemical processes is obtained by applying ABC method. The environmental indices-based approach according to WAR algorithm method has been extended into general environmental factor by Biwer and Heinzel [19] for SHE assessment of early development of a chemical process. This environmental factor is originated from six impact groups containing impact categories, as shown in figure 4-8 below.

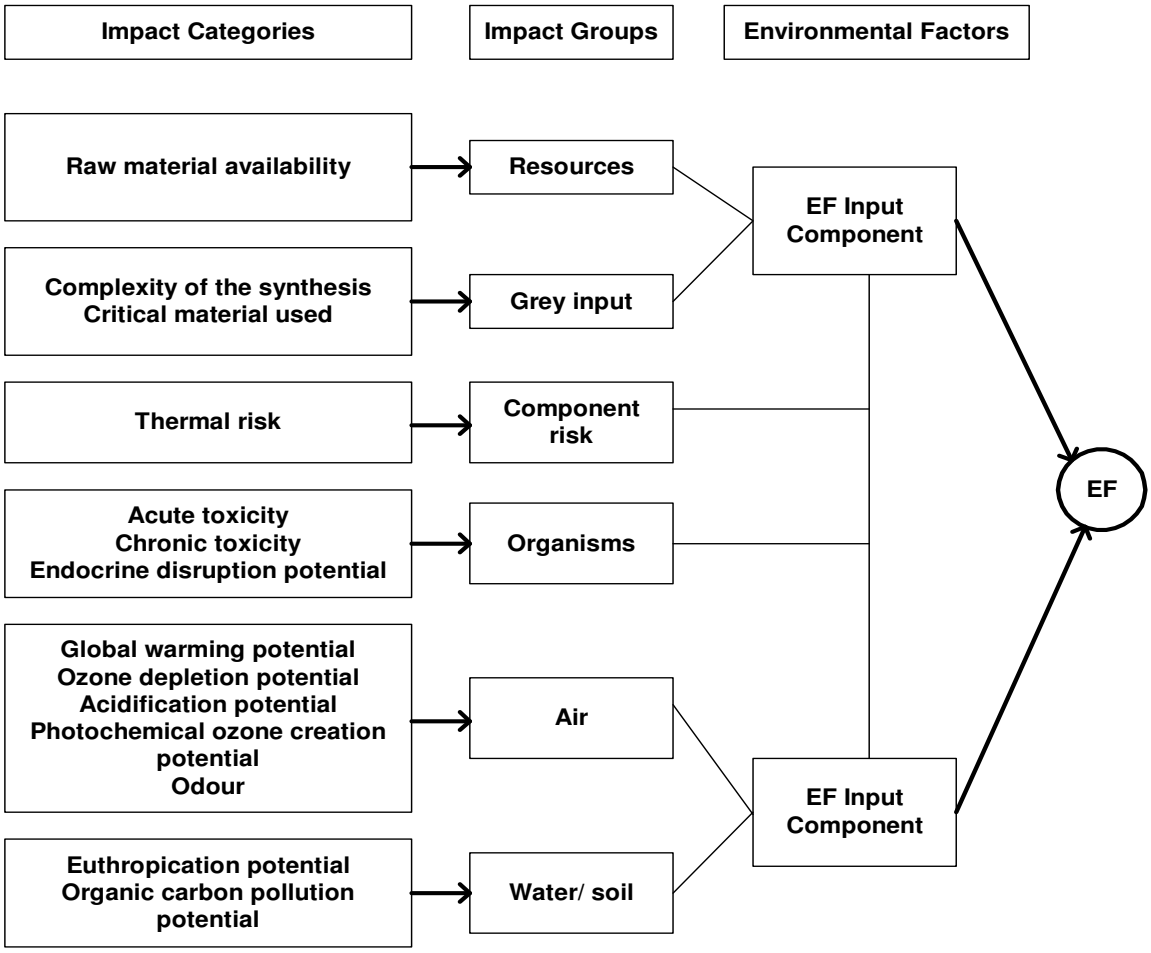


Figure 4-8. Classification of Environmental Impact Factor [16]

The term of ABC denotes the classification of the environmental, safety and health categories associated with components and process as well as the availability of resources. Class A characterizes serious problems which may later on stop process development or may create large costs. Class C is noncritical and class B is somewhere in between [65]. If there are not any data available, then the material is assigned first to the class A [2]. All classification is based on best-available knowledge and may therefore change in the future.

The material indices are derived form input and output balances. A mass loss index is defined as [67]:

$$MI_i = \frac{m_i}{m_p} \qquad (4\text{-}22)$$

where m is the mass flow of component i or the product p. This index state how much a component of the balance per unit product is used and/or resulted. Considering all mass flow, a mass index, MI, is then defined as [67]:

$$MI = 1 + MI_i \quad (4\text{-}23)$$

MI represents the total mass of input needed for unit mass of product.

For providing all values for developing an overall view of environmental index, the weighting factor (*w*) is calculated using following equation [67]:

$$w = B^{\alpha} \quad (4\text{-}24)$$

where *B* is the default basis (normally 10) and α is the exponent determined by the class membership (α = 0,1 or 2 for class A, B or C respectively). The classification of class membership is defined in table 4-13. Then, environmental index is calculated as follows [2]:

$$EI = \frac{\sum_{1}^{j}\sum_{1}^{i} IC_j \cdot w_{i,j} \cdot MI_i}{\sum_{1}^{j} IC_j} \quad (4\text{-}25)$$

where $w_{i,j}$ is weighting factor from ABC classification of material in impact category, IC_j is weighting factor of an impact category for weighting of the individual category. Then, the impact potential of environmental index is finally calculated as follows[2]:

$$EI_i = \frac{\sum_{1}^{j} IC_j \cdot w_{i,j}}{\sum_{1}^{j} IC_j} \cdot MI_i \quad (4\text{-}26)$$

The impact potential of all materials in an impact category was given as [2]:

$$IP_i = \frac{\sum_{1}^{j} IC_j \cdot w_{i,j} \cdot MI_i}{\sum_{1}^{j} IC_j} \quad (4\text{-}27)$$

Table 4-13. Valuation of impact classification for ABC models (adapted from [67])

Impact category	I/O	Class A	Class B	Class C
Land use (LU)	I	≥ 100 m^2 kg^{-1}	≥ 10 m^2 kg^{-1} and < 100 m^2 kg^{-1}	< 10 m^2 kg^{-1}
Raw material availability (RMA)	I	Only fossil, predicted exhaustion within 30 years	Only fossil, predicted exhaustion in 30–100 years	Exclusively renewable, or guaranteed long term supply (>100 years)
Complexity of the synthesis (CS)	I	> 10 synthesis steps	3 – 10 synthesis steps	< 3 synthesis steps
Thermal risk (fire and explosion) (TS)	I	R: 9,11,12,14-19,30,44	R : 10	No or very low fire and explosion risks
Acute toxicity (AT)	I	R 23-29, 31, 31, 35, 39, 42, 43, 50; Reference: T+, T; CH-toxicity:1,2	R 20-22, 34-38, 41,63,65-67; References: Xn, Xi, C, CH-toxicity:3,4	C-H toxicity: 5 or free
Chronic toxicity (CT)	I	MAK:< 1 mg/m^3; R 33,40, 45-49; 60,61,64,	MAK:< 1-10 mg/m^3; R 53,58, 60,62	MAK:> 10 mg/m^3
Biological risk (BR)	I/O	Biomaterial: RG 3 or RG 4; GenTG: S3 or S4	Biomaterial: RG 2 ; GenTG: S2	Biomaterial: RG 1; GenTG: S1
Ecotoxicity (ET)	I/O	R 50; WGK 3	R 52, 52, 54 -57; WGK 2	WGK 1 or no water risk
Global warming potential (GWP)	O	GWP > 20	GWP < 20	No GWP identified
Ozone depletion potential (ODP)	O	ODP > 0.5	ODP < 0.5	No ODP identified
Acidification potential (AP)	O	AP > 0.5	AP< 0.5	No AP identified
Photochemical ozone creation potential (POCP)	O	POCP > 30 or NO_X	2 < POCP < 30	POCP < 2 or no impact identified
Odour (Od)	O	Odour shrinking values < 10 mg/m^3	Odour shrinking values < 500 mg/m^3	Odour shrinking values> 500 mg/m^3 or no odour
Euthropication potential (EP)	O	Nitrogen-content > 0.2 or Phosphor-content > 0.05	Nitrogen-content > 0.05 or Phosphor-content > 0.01 or Carbon-content > 0.2	Free of Nitrogen-content and Phosphor-content

Note: ThOD = Theoretical Oxygen Demand; COD = Chemical Oxygen Demand; EU = EU classification; R = R-codes; CH-poison class = Swiss poison classes; ERPG = Emergency Response Planning Guidelines (American Hygiene Association); IDLH = Immediately Dangerous to Life and Health (National Institute for Occupational Health and Safety); LC, LD = Lethal Concentration/Dose; MAK = German workplace threshold value (Maximale Arbeitsplatzkonzentration); IARC = classification of International Agency for Research on Cancer; Unit Risk: cancer risk (US Environmental Protection Agency); NFPA = hazard classes US National Fire Protection Agency (H = Health, F = Flammability, R = Reactivity); fp = flash point; ait = auto ignition temperature; T decomp = decomposition temperature; log (λ) = logarithm of electric conductivity; WGK = German water hazard classes (Wassergefährdungsklassen)

Table 4-14. Example of valuation of weighting values of the problem as well as impact categories and problem classification [67]

Input-Impact categories	**Weighting value**	**Category (SHE)**
Thermal Risk	100	S
Acute toxicity	100	H
Chronic toxicity	100	H
Biological risk	100	H
Land use	90	E
Raw material availability	75	E
Complexity of the synthesis	50	E
Sum	615	
Output impact category	**Weighting value**	**SHE**
Thermal Risk	100	S
Acute toxicity	100	H
Chronic toxicity	100	H
Biological risk	100	H
Ecotoxicity	80	E
Global warming potential	100	E
Ozone depletion potential	66	E
Acidification potential	66	E
Photochemical ozone potential	33	E
Odour	33	E
Euthropication potential	75	E
Sum	853	

From those equations, the environmental impact has relative measures on detrimental impact into the environment. The higher the environmental index means the higher potential impact to the environment.

As an illustrative example, a biosynthesis of (R)-1-4-Chlorpheniyl-ethanol is considered. This biosynthesis is taken place in two-phase ionic liquid/phosphate solution. The detail explanation regarding the process can be found in Heinzle, Biwer and Abdul Kholiq [67]. The design alternatives are shown in figure 4-9. The first alternative (alternative A) considers the use of recycling stream while the second alternative (alternative B) considers the use of centrifugation, as shown in figure 4-9.

All streams entering and leaving are assessed using ABC methods. First, relevant categories of problems are identified to characterise possible impacts on the safety, health and environment (SHE). The classification of environmental categories follows the values in table 4-14 and the ABC classification follow the table 4-13. Simulation has been run by Super-Pro designer simulation tool and generated mass and energy balances.

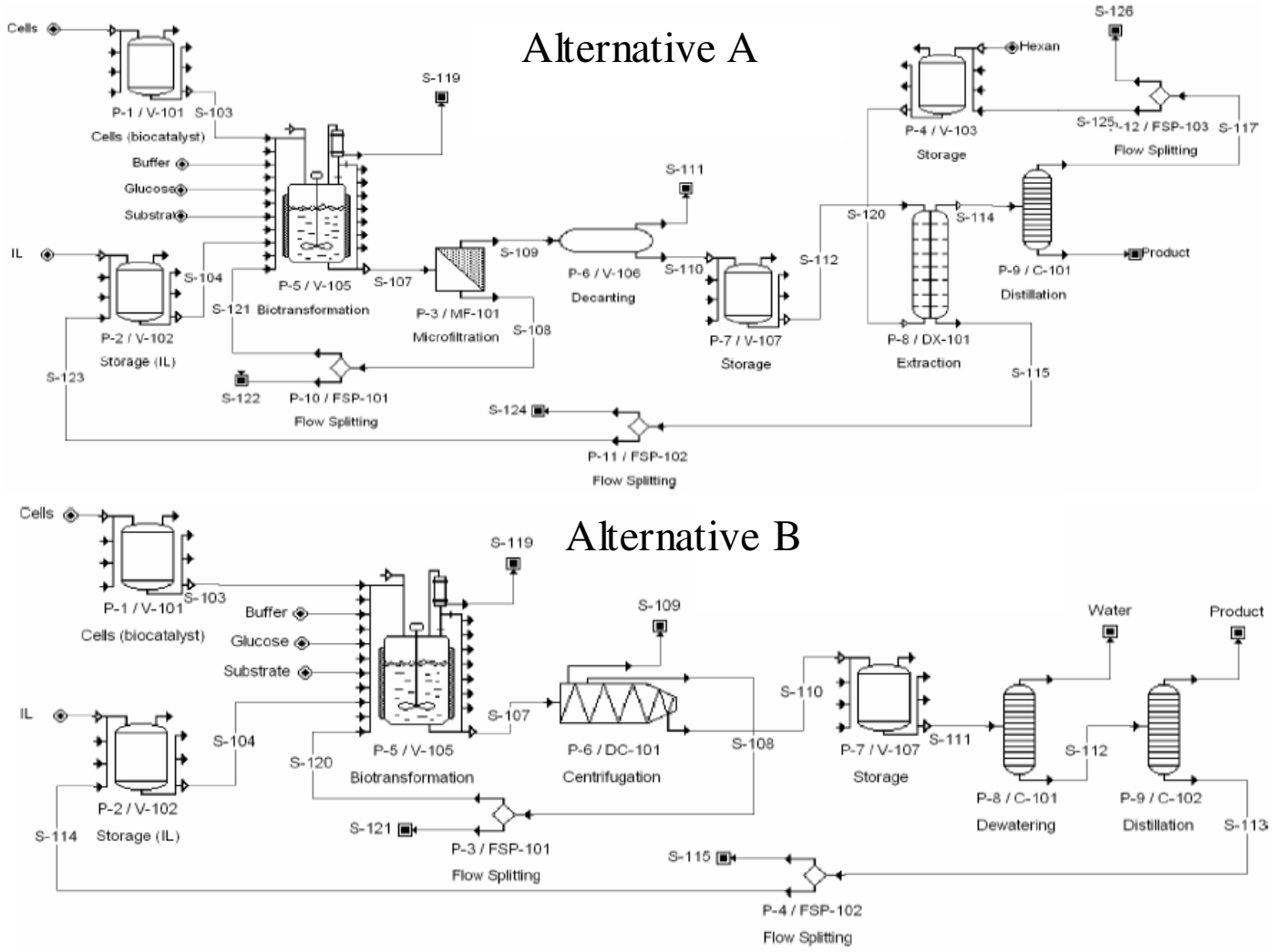


Figure 4-9. Alternatives of flowsheet designs for biosynthesis of ionic liquid [2]

For the first qualitative evaluation, the materials with A-class are analysed first. From the input and output materials (except product) altogether seven materials are at least once classified as A-class. The used ionic liquid has the classification A-class in the two categories chronic and ecotoxicity. The extracting agent hexane has thermal risks and chronic toxicity the classification A-class in the two categories. Because of the nitrogen and/or phosphor content, three materials (biomass and the two phosphate salts) are classified in the category euthropication under the A-class.

Acetic acid belongs in the two categories acute toxicity (R-35 - causes heavy skin irritation) and odour to the A-class. Ethanol has thermal risks then is classified in the A-class. It is to be noted that the ABC classification means a view of materials in its pure form. Since acetic acid and ethanol appear as by-products in very low concentration, the respective A-class has here practically no meaning.

1-butyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]amide (abbreviated as [Bmim][Tf2N]) has the category of chronic toxicity due to uncertain data situation and the comparability of the LC_{50}-value (from provisional investigations with *Daphnia magna*) with organic solvents, therefore it is classified as the A-class. Considering the uncertain data situation in the safety sheets for the classification of 1-butyl-3-methyl-imidazolium tetrafluoroborate ([bmim][BF4]) and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) regarding the water hazard class (or *WGK*: *Wasser Gefährdung Klasse*) 3 then BMIM[Tf2N] is classified in the category ecotoxicity under the class A.

The ionic liquids do not have a measurable steam pressure as low melting salts, thus do not form into gas phase at that condition. Therefore they are classified as the class C for the following categories: global warming potential (GWP), ozone depletion potential (ODP), photooxidation ozone creation potential (PCOP), acidification potential (AP) and odour. Table 4-15 shows the ABC classification of other materials.

Table 4-15. Example of ABC classification of the ionic liquid separation process [67]

Components		**LU**	**RMA**	**CS**	**TR**	**AT**	**CT**	**BR**	**ET**	**ODP**	**AP**	**PCOP**	**Od**	**EP**
		I	**I**	**I**	**I/O**	**I/O**	**I/O**	**I/O**	**O**	**O**	**O**	**O**	**O**	**O**
4-Cl-AP	IO	C	B	C	C	B	B	C	C	C	C	C	C	B
Acetic acid	O	NR	NR	NR	B	A	C	C	C	C	C	C	A	B
Biomass	IO	B	C	C	C	C	C	C	C	C	C	C	C	A
BMIM[TF2N]	IO	C	B	B	C	C	A	C	A	C	C	C	C	B
CO2	O	NR	NR	NR	C	C	C	C	C	C	C	C	C	B
Ethanol	O	NR	NR	NR	A	C	C	C	C	C	C	B	B	B
Glucose	IO	B	C	C	C	C	C	C	C	C	C	C	C	B
Hexan	O	C	B	C	A	B	A	C	C	C	C	C	C	B
Lactic acid	IO	NR	NR	NR	C	B	C	C	C	C	C	C	C	B
KH2PO4	IO	C	C	C	C	C	C	C	C	C	C	C	C	A
K2HPO4	IO	C	C	C	C	C	C	C	C	C	C	C	C	A
Water	IO	C	C	C	C	C	C	C	C	C	C	C	C	C

LU: land use, RMA: raw material availability, CS: complexity of the synthesis; TR: thermal risk; AT: acute toxicity; CT: chronic toxicity; BR: biological risk; ET: Ecotoxicity; ODP: ozone depletion potential; AP: acidification potential; PCOP: photochemical oxidation potential; Od: odour; EP: euthropication potential.

Then, the weighting factors can be calculated using equation 4-24 above. From the mass balance, the mass indices is calculated using equation 4-23 and the environmental index is calculated using equation 4-25. Figure 4-10 shows the mass indices and environmental indices calculation for all alternatives. The results show that alternative B (the process with

centrifugation) gives significant reduction on environmental impact of detrimental effects of the process to the environment.

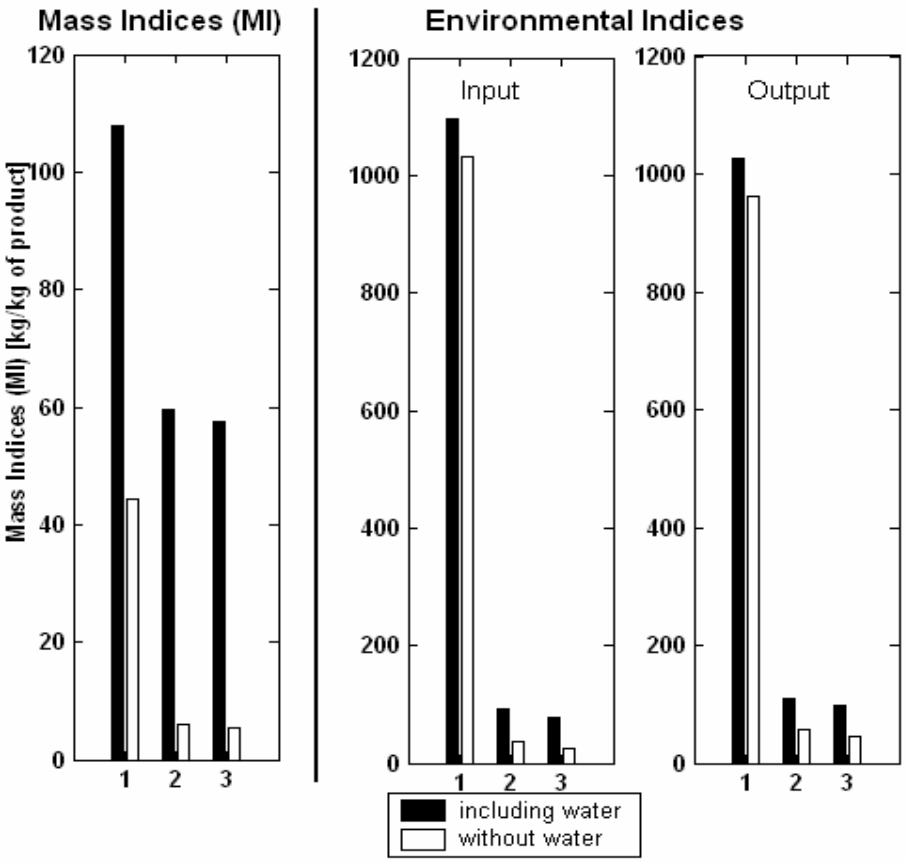


Figure 4-10. Mass indices of input and environmental indices of input and output either including water and without water for all process models. The number of 1, 2 and 3 denotes basis model, alternative A (with recycling) and alternative B (with centrifugation), respectively

4.4. Safety criteria

The results of a major industrial accident can be devastating, such as the Flixborough, England accident, which cost the lives of 28 people, the whole plant and many injuries; the Bhopal, India accident, which killed more than 5000 civilians and injured 15,000 more; a massive explosion in Pasadena, Texas on Oct. 23, 1989, resulted in 23 fatalities, 314 injuries, and capital loss of over $715 million [129] . These are extreme cases of major accidents in the process industry, but minor incidents are more common [129].

An investigation of accidents shows that there is a chance to reduce frequency and/or damage. Then, there is a necessity of safety and risk analysis in chemical industries to support. The logical tree for common risk assessment follows following steps as shown in figure 4-11 [127]:

- reveal weaknesses of the plant
- identify and describe relevant sequences of events
- quantify frequencies of releases related to their consequence-potential
- investigate safety gains from various possible system modifications and
- improve the system if necessary (either alone or in combination with others).

4.4.1. Risk analysis/ assessment

Three main activities in safety/ risk analysis are hazard identification, risk assessment and accident prevention. Hazard is the potential of incident. In chemical process, a hazard can arise e.g. from toxicity of materials or release of energy. According to Steinbach, Antelmann and Lambert [127], some of indices have been introduced by chemical industries for identifying hazard level, among which are Dow fire and explosion index, Mond index and Instantaneous Fractional Annual Loss (IFAL), as tabulated in table 4-16 below.

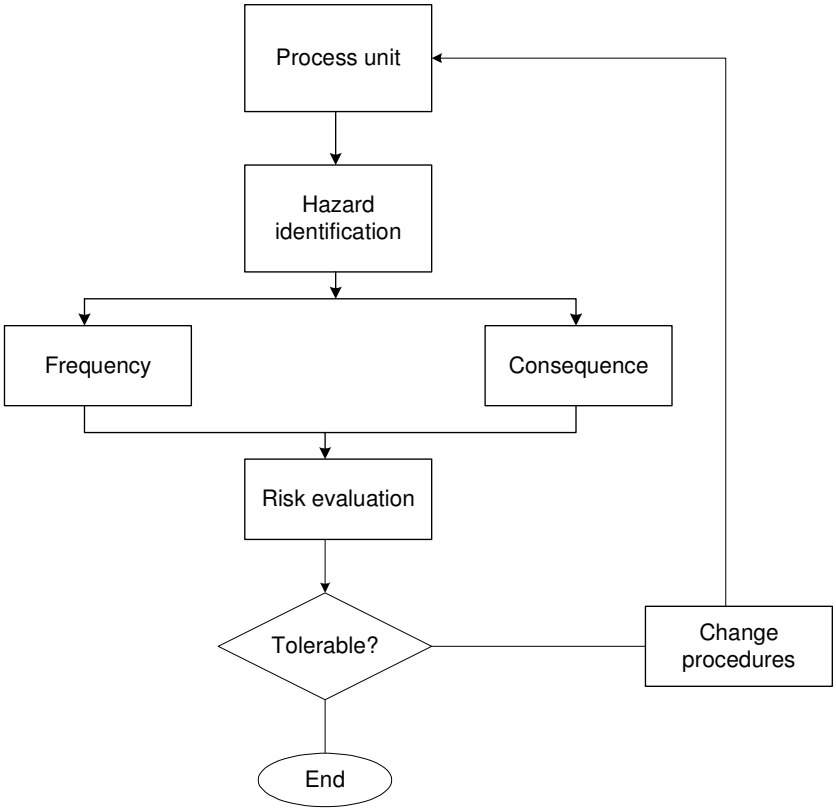


Figure 4-11. Logical tree for common risk assessment

Table 4-16. Most popular hazard indices [127]

Hazard Indices	Description
Dow Fire and Explosion Index (F&EI)	It was first developed by the Dow Chemical Company in 1964. Indices are based on material properties, process conditions, areas of exposure, and other damage factors to derive the base maximum probable property damage (MPPD).
Mond Index	It is an extension of the Dow F&EI index with some additional considerations. Initial assessments of fire, explosion and toxicity are carried out for each process unit and then combined with special indices. Eventually, an overall risk rating is derived from individual fire, explosion, and toxicity indices.
Instantaneous Fractional Annual Loss (IFAL)	It was originally developed for insurance assessment purpose by the Insurance Technical Bureau. Use frequency and size of potential emissions and chance of ignition to determine damage. It determines contribution of each major item of process equipment according to process factors, engineering factors, and management factors.

Risk is defined as a measure of e.g. human injury, environmental damage, or economic loss in terms of both the incident frequency and the magnitude of the injury/ damage/ loss [116]. Risk is the product of the frequency of an incident times consequence (damage) of incident, as formulated in equation 4-28 [116].

$$Risk = f(s, c, F) \qquad (4\text{-}28)$$

where s, c and f stand for scenario, consequence and frequency respectively.

The risk level is very often represented in a matrix-based, called risk (potential) matrix as shown in figure 4-12. Each point in the matrix correlates a value from probabilistic and subsequent consequence levels. With this risk matrix, the area of acceptable risk level limit is shown [127].

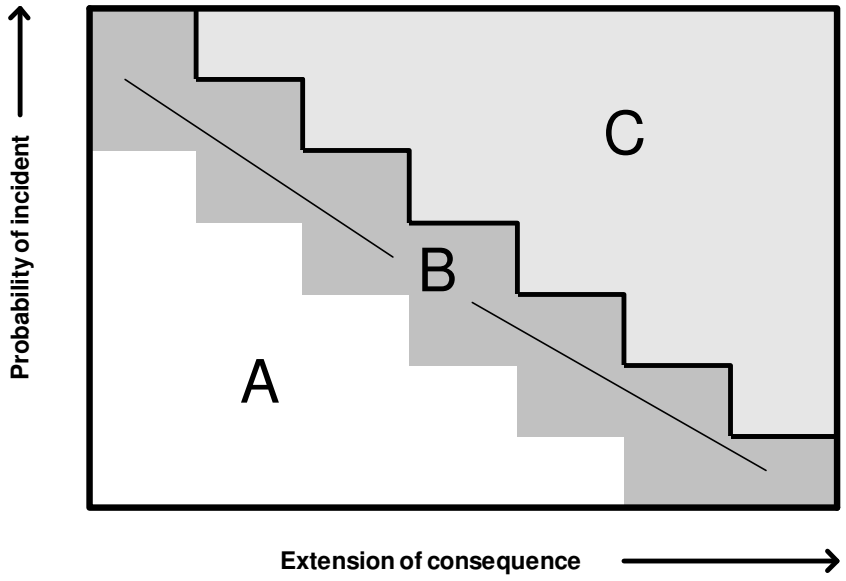


Figure 4-12. Risk Potential Matrix. The region under "A" denotes the are for acceptable scenario, "B" denotes the are that requires further analysis and "C" denotes the area for unacceptable scenario

A variety of techniques have been used for risk analysis in the CPI including Safety Review, Checklist Analysis, Relative Ranking, "What-if" Analysis, Preliminary Hazard Analysis, Hazard and Operability Study (HAZOP), Failure Modes and Effects Analysis (FMEA), Fault Tree Analysis (FTA), Event Tree Analysis (ETA), Cause-Consequence Analysis (CCA), Human Reliability Analysis (HRA). Brief overviews of three methods will be discussed in the next paragraph, namely FMEA, ETA and FTA [127].

4.4.1.1. Failure modes and effects analysis (FMEA)

FMEA is a systematic procedure in which each equipment failure mode is examined to determine its effects on the system and classify it according to severity and criticality. FMEA is an inductive method oriented toward equipment rather than process parameters. All of the failure modes for each item of equipment are tabulated with their effects, safeguards, and related actions listed. An FMEA is especially useful to identify single failure modes that lead to an incident directly, while it is not powerful to identify combinations of equipment failure and human errors as risk contributors [127].

An example of FMEA data base is shown figure 4-13. This FMEA data base will help to systematically examine possible process failure, then to redesign in order to eliminate the possibility of failure.

PLANT AND PROCESS DOCUMENTATION									
Description of function:						Raw data/ process:			
Recent condition						Modified condition			
Type of disturbances	Possible problem	Failure identification	Framework of response	Effect identifi-cation	F C	Framework of modification	Corrective action	Effect identification	F C
TECHNICAL FAILURE ANALYSIS		SYSTEM ANALYSIS		EFFECT ANALYIS		SYSTEM OPTIMISATION		EFFECT ANALYIS	

Figure 4-13. FMEA data base for plant and process [22]. Note: F: Frequency ; C: Consequence

4.4.1.2. Event tree analysis (ETA)

An event tree is an inductive reasoning process that starts with an initiating event followed by the binary success or failure of subsequent safeguards, human responses, and other safety measures to determine its possible outcomes. It is especially suitable to find possible outcomes of particular initial events and their respective probabilities with the data for initial events and subsequent protections and procedures [127] .

Typically, an event tree is constructed into “success tree (the tree above the decision tree)” and “failure tree (the tree below the decision tree)”. An illustrated simple example of event tree for an initiating event “A” is shown in figure 4-14 below. The system has three components to handle such system failure, namely component 1, component 2 and component 3. If the event A is not notified, the system will be mostly contained in the component 1. If the component 2 fails as well, the system will be failure, with the frequency of its failure equals to 0.0001.

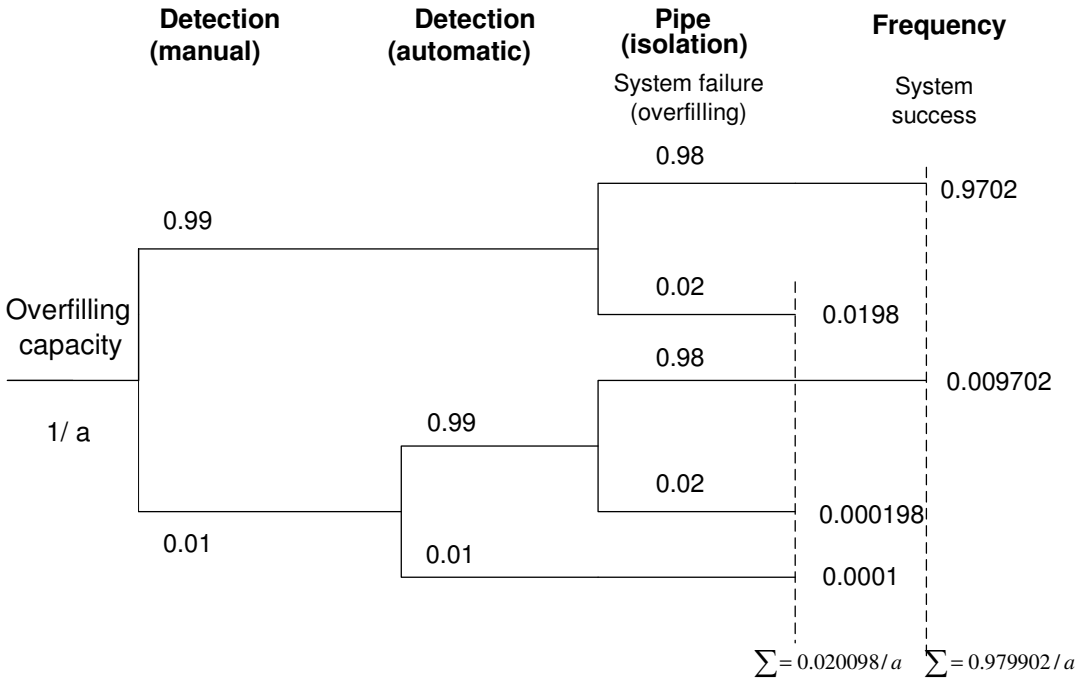


Figure 4-14. Example of simple event tree

4.4.1.3. Fault tree analysis

Fault tree analysis was first developed in 1961 at Bell Telephone Laboratories for missile launch control reliability during the Polaris project, and has long been adapted for application in the chemical process to predict the likelihood of hazardous incidents and to identify major risk contributors [127]. As an illustration, figure 4-15 is depicted for fault tree scenario for the systems of two pump and one valve.

One major barrier with regard to its application in the chemical process industry (CPI) is fault tree construction. Processes, materials, equipment, and control mechanisms are much more diverse in the CPI than in the nuclear industry. The method does not itself assure that all failure modes have been considered. It requires specially trained and skilled practitioners who are familiar with the methodology and understand the process under analysis to ensure the completeness and correctness of the analysis. Fault trees for a reasonably complicated process will be enormous and needs overwhelming expert time, sometimes measured in years, to complete. Due to the human labour and time required, the cost is relatively high compared to other methodologies [127].

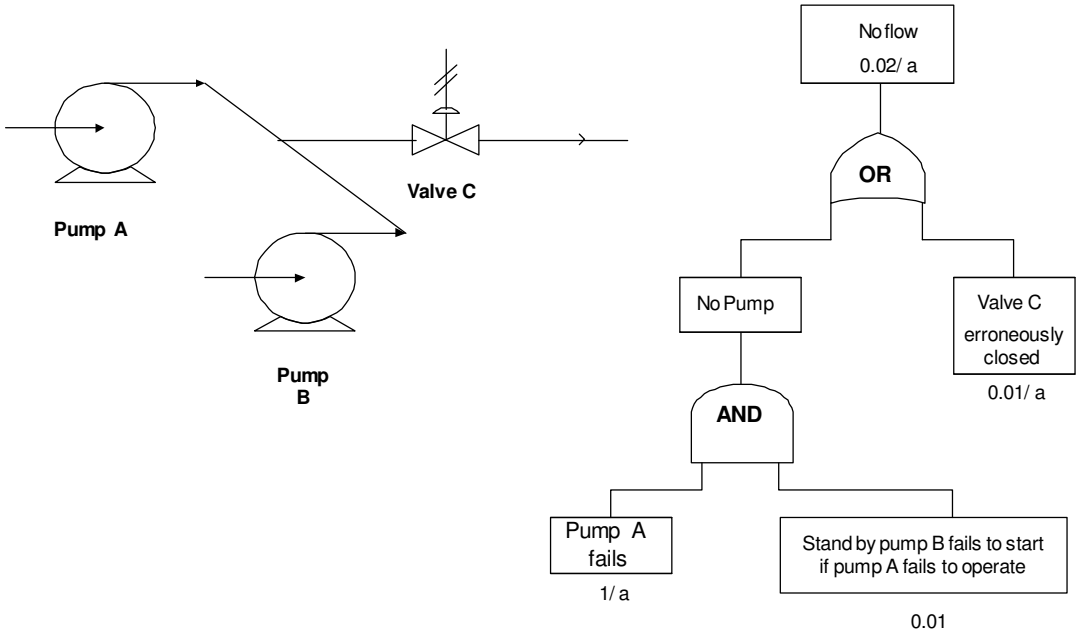


Figure 4-15. Example of fault tree diagram for two pumps and one valve

4.4.2. Accident statistics

There are significant numbers of safety related disturbances in recent years. Based on Kister's surveys on column malfunction histories [83],[86], the hazards in distillation are emerged from high material contents and equipment complexity. The malfunction report in the number of the main causes of accidents is depicted in figure 4-16. Column internal and instrument and control problems are at the top causes of column malfunction. Common symptoms and root causes of accidents are listed in the table 4-17.

According to Kister's report [86], the most important effects that must be investigated in distillation column are:

- Influence of the hydrodynamic mass transfer
- Control loop stability during non standard operation
- Effects of operational conditions on process safety
- Effectiveness of the protective systems

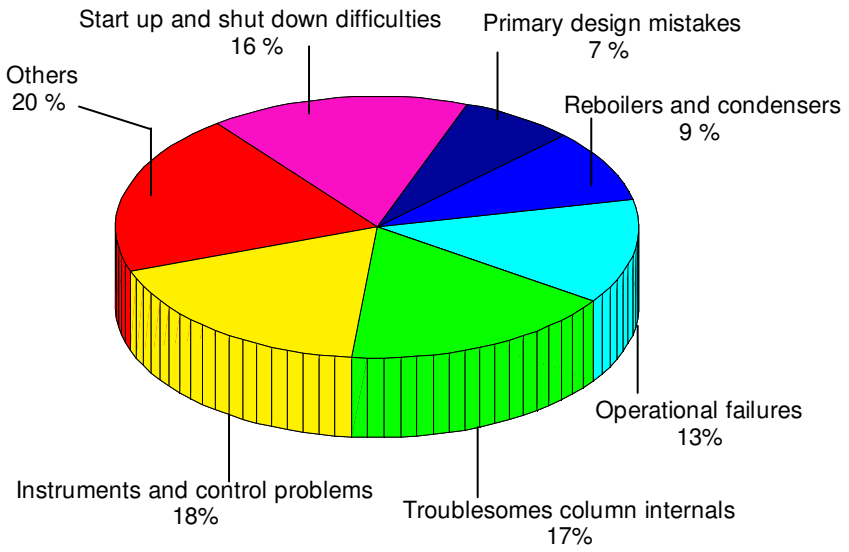


Figure 4-16. A Report on distillation malfunction histories [86]

Table 4-17. Common symptoms and root causes in distillation malfunction [86] ,[87]

Symptoms	Root Causes
Instrument reading do not agree with other observations	▪ Incorrect transmitter range specified ▪ Two phase flow through flow meter or control valve ▪ Incorrectly installed or specified instruments
Equipment underperforms	▪ Hand-operated valves in wrong position ▪ Exchanger of equipment fouled
Inadequate flow	Unexpected two-phase flow, fouling in piping or equipment, pump related problems (eg: cavitation)
Temperature control problems	Damage insulation, poor controller tuning, unexpected heat of reaction
Premature column flooding	Internal damage/ fouling, foaming problem, instable control system, presence second liquid phase
Low heater efficiency	High combustion air flow, heat leaks in system
Product contamination	Leaking valves, corrosion product presence

4.4.3. Previous research in safety assessment

Can [26] described a safety assessment method using Failure Mode and Effect Analysis (FMEA) in combination with event tree analysis (ETA) and process disturbances simulation. The event tree analyses (ETA) starts from a defined initiating event and identifies potential consequences in a systematic way. The FMEA method requires raw data regarding explanation of the system/ equipment function, fault-effect analysis, valuation of weak point (risk potential), weak point elimination if necessary, as shown systematically in figure 4-17.

According to Can [26], the framework of risk assessment is originated from the definition of initiating event and top event then the probability as well as the consequence are assessed and listed in a table. The consequence addresses the intensity of side effect from particular system (e.g. effect to the environment). The general criteria of consequence are expressed qualitatively from "very good" implying that the improvement is not urgent to be applied, until "bad" condition of the system.

The valuation and the description of consequence is shown in table 4-18. Whereas, the valuation of the frequency is started from 1 (very low, probability ≡ 10^{-7}/y) and ended with 9 (very high, probability ≡ 10/y), as shown in table 4-19. Then, the combination of probability and consequence value results in the Risk Potential Index (RPI) which has significant meaning for the priority of improvement of a definite plant that can be plotted in RPI Matrix. There are 3 region in RPI matrix, acceptable region, not acceptable region and acceptable region but with further evaluation or optimisation.

Table 4-18. Valuation of consequence [26]

Consequence Value	General Description
1 – 3	Good
4 – 5	Satisfied
6 – 9	Bad

Table 4-19. Valuation of probability [26]

Probability Value	Frequency	Probability
1	10^{-7}/ Year	Very low/ implausible
2	10^{-6} / Year	Low
3	10^{-5} / Year	
4	10^{-4} / Year	Moderate
5	10^{-3} / Year	
6	10^{-2} / Year	High
7	10^{-1} / Year	
8	1 / Year	Very high
9	10 / Year	

In order to characterise the effect of different operational disturbances, the dynamic modelling of the column can be used for safety assessment taking into account that the malfunction is considered as reducing the optimum condition. Detailed dynamic simulation of operational failure (i.e. column malfunction) gives information concerning internal process behaviour. According to figure 4-17, the whole possible different operational failures will be

included in FMEA data base. With the aid of this data base, risks can be assessed for normal operational states as well as in case of operational failures. Furthermore, the strategy will be applicable for the preventive measures or 'early warning systems' as well as incident avoidance.

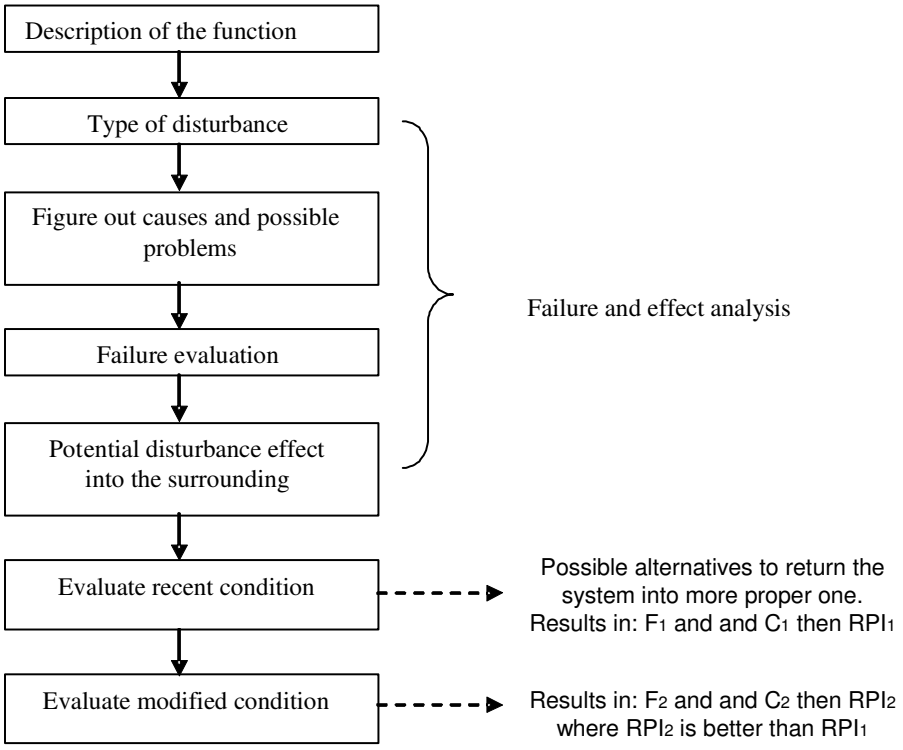


Figure 4-17. Steps for systematically development of FMEA data base [26]

4.4.4. Inherent safety

The concept of "inherently safer" design was evolved by Kletz [89]. This concept implies that the process relies on naturally occurring phenomena and robust design to avoid hazardous events or situations. The basic idea is to develop chemical processes that are fundamentally safer through the strategies below:

1. Substitution. It means the use of less toxic or dangerous chemicals.
2. Attenuation or moderation. It means the use of hazardous chemicals under less hazardous condition.
3. Limitation. It means the use of designs that limit the effect of equipment failure with reduced dependence on instrumentation and protective equipment.
4. Intensification. It means the use of smaller liquid holdups, or less material to explode.

These principles help to avoid or reduce hazards by using safer materials and operating conditions, minimising inventory, and by designing a simpler and friendlier plant. The lists of principles have been extended by Kletz [89] to include other aspects that make plants friendlier by reducing error opportunities or reducing the plant sensitivity to errors and abnormal situations. The principles for inherently friendlier plants include the following [89]:

1. Simplification. It means designing simpler plants that give fewer opportunities for error or wrong operation
2. Avoiding knock-on effects. It means designing plants in such a way, so that when incidents occur the domino effects do not happen.
3. Making incorrect assembly impossible. It means assembling something in more than corrected way so that errors and accidents are prevented.
4. Making status clear. It means equipping plants to allow the understanding of their status.
5. Tolerance. It means developing safer plans in such a way so that forgive operator errors, poor installation and equipment failures.
6. Ease of control. It means simplifying a plant by fewer instruments required.
7. Software. It means simplifying the software to use and understand. Is should be homogeneous for all plant control systems.

In addition, Kletz [89] introduced the relation between the principles of inherent safety and pollution prevention. Kletz argues that when a plant is designed to reduce or eliminate the hazards, not only does it become safer but possible emissions to the environment are also reduced or eliminated. Therefore, the environmental damage resulting from the release of chemicals during an incident can be significantly reduced. Moreover, contamination associated by releases or leaks occurring during normal operations is also reduced because the quantities of chemicals or their hazards are limited.

Heikkilä [63] developed the Inherent Safety Index (ISI) based on the Chemical Inherent Safety Index (I_{CI}) and the Process Inherent Safety Index (I_{PI}). The indices represent major inherent safety factors, as listed in table 4-20. The Chemical Inherent Safety Index describes chemical aspects of inherent safety, and the Process Inherent Safety Index represents the process related aspects. Inherent Safety Index (I_{ISI}) is a sum of the Chemical Inherent Safety Index (I_{CI}) and the Process Inherent Safety Index (I_{PI}) as summarized as follows:

$$I_{ISI} = I_{CI} + I_{PI} \quad (4\text{-}29)$$

The Chemical Inherent Safety Index (I_{CI}) contains chemical factors affecting the inherent safety of a process. These factors consist of chemical reactivity, flammability, explosiveness, toxicity and corrosiveness of the chemical substances present in the process. Flammability, explosiveness and toxicity are determined separately for each substance in the process. Chemical reactivity consists of the maximum values of indices for the heats of both main and side reactions, and the maximum value of chemical interaction, which describes the unintended reactions between chemical substances present in the process area studied.

$$I_{CI} = I_{RM,\,max} + I_{RS,\,max} + I_{INT,\,max} + (I_{FL} + I_{EX} + I_{TOX})_{max} + I_{COR,\,max} \quad (4\text{-}30)$$

The Process Inherent Safety Index (I_{PI}) expresses the inherent safety of the process itself. It contains the subindices of inventory, process temperature and pressure, equipment safety and safe process structure.

$$I_{PI} = I_I + I_{T,\,max} + I_{p,\,max} + I_{EQ,\,max} + I_{ST,\,max} \quad (4\text{-}31)$$

Most of the subindices of the method can be estimated quite easily by using physical or chemical properties of compounds present, or based on operating conditions and a concept of the process. For the index score list, the reader should refer to Heikkilä [63].

The value of indices or score is distinguished based on particular range in an equipment, unit or process. For example, a unit with the process pressure of 1-5 bar will be scored of 0, 5-25 bars will be 1, 35-30 bars will be 2, and so on. Further scoring technique for inherent safety indices is referred to Heikkilä [63]. Thus, the inherent safety subindex will give better view which equipment or process has inherently safer design. An example of scoring technique in distillation column is tabulated in table 4-21 below. Inherent safety analysis for distillation unit with the temperature of 155° C, pressure maximum of 4 bars and is aimed to separate some acids. Then, the table of inherent safety analysis is given below:

Table 4-20. Inherent safety index and its subindices [63].

Chemical inherent safety index	Process inherent safety index
Subindices for reaction hazards	***Subindices for process condition***
Heat of the main reaction, I_{RM}	Inventory, I_I
Heat of side reactions, I_{RS}	Process temperature, I_T
Chemical interaction, I_{INT}	Process pressure, I_P
Subindices for hazardous substances	***Subindices for process system***
Flammability, I_{FL}	Equipment, I_{EQ}
Explosiveness, I_{EX}	Process structure, I_{ST}
Toxicity, I_{TOX}	
Corrosiveness, I_{COR}	

Table 4-21. Inherent safety analysis of distillation column [63]

Inherent safety criteria	Description	Score
Chemical inherent safety index		
Heat of main reaction	No reaction	0
Heat of side reaction, max	No side reactions	0
Flammability, explosiveness, toxicity	Maximum sum for acetic acid	7
Corrosiveness	Stainless steel	2
Chemical interaction	Worst interaction: Methyl iodide – hydriodic acid	4
		$\sum = 13$
Process inherent safety index		
Inventory	100 t/h	3
Process temperature, max	155° C	2
Process pressure, max	4 bar	0
Equipment	Distillation tower	1
		$\sum=6$
Total inherent safety index		**19**

4.5. Controllability criteria

The justification of process control in the context of business decision-making may include the following economic or operating considerations: increased product throughput, increased yield of higher valued products, decreased energy consumption, decreased pollution,

decreased off-specification product, improved safety, extended life of equipment, improved operability, and decreased production labour [60]. Therefore, there has been the opportunity to connect controllability to profitability.

According to Gollapalli, Dantus and High [60] the term of controllability qualitatively means:

- how well the process rejects disturbances
- how severely multiple variables interact
- how easily the system moves from one operating condition to another.

Traditional to process control normally perform controllability in analysing a given process configuration to find the best selection of pairing controlled and manipulated variables and to find the controller parameters with the best closed loop performance. In practice, this means that when the plant is subject to disturbances it will still operate within an acceptable distance from the optimum, and there is no need to re-optimise when disturbances occur.

The main idea behind controllability analysis is that how to integrate significant changing with respect to improvement of economic performance with resulted controllability. It means, the main objective in optimising controllability aspect is to find a best compromise solution among the economic and controllability objectives by applying a multiobjective optimisation algorithm which considers quantitative trade-offs.

This is due to the fact that changing design will have significant impact on controllability. Previously, the paradigm regarding design and control has set controllability only sequentially, that is economically optimum process configuration is known earlier than examination of controllability. Since the significant economic impact of design on controllability, therefore integrating controllability and economic consideration simultaneously is a challenging issue in control design field.

The work on controllability is to find quantitative controllability measures while requiring not extensive amount of analysis. The starting point for controllability analysis is Multiple Input Multiple Output (MIMO) system [100], [102]:

$$y(s) = G(s) \cdot u(s) + Gd(s) \cdot d(s) \qquad (4\text{-}32)$$

where
- y(s) : output variables
- G(s) : process transfer function matrix
- Gd(s) : disturbances transfer function matrix
- d(s) : disturbances

5. Case Study

5.1. Methodology for case study

The systematic procedure to solve multicriteria problems in this work is shown in the block diagram in figure 5-1. The procedure starts from the definition of improvement target. This step consists of definition of the scope of investigation and system boundaries as well as improvement targets. Then, a process model is created and followed by generation of alternatives for comparison of several decision alternatives regarding the designs, control structures, and decision variables of the investigated plant/ process. Each alternative is modelled using Aspen Plus. Then, ASPEN Plus will solve material and energy balances of the simulated plant.

The evaluation procedure is started by defining the target of improvement for design alternatives. Then, a process simulation model is run for each design alternative. The simulation is performed using ASPEN Plus for steady state simulation to generate mass and energy data and ASPEN dynamic for dynamic simulation to generate data for dynamic behaviour performance.

The economic effectiveness of a design alternative is evaluated by applying attributes of economic potential. In this way, the economic potential will provide important information about the design alternative in terms of which operation of a design alternative is comparatively more profitable than others thereby helping to define design targets as well as to generate better design alternatives.

The analysis of environmental criteria relies on heat and mass balance generated from ASPEN Plus. The results from mass and energy balances are transformed into environmental impact information after applying some description of limiting values imposed by regulation or decision maker. Through the graphical user interface (GUI) of waste reduction algorithm from United State – Environmental Protection Agency [106], the framework of potential environmental impact (PEI) of design alternatives can be obtained. The calculation of PEI is described in chapter 4. The framework of potential environmental impact is used to compare both design alternatives with respect to environmental criteria. All potential impacts will be tabulated, so that can give clear impression regarding which components or stream gives significant impact into the environment.

For safety criteria, this thesis will follow a method according to Can [26]. The assessment methodology relies on the evaluation of frequency and consequence associated with the disturbances in distillation unit. The term of inherent safety according to Heikkila [63] will be applied in order to assess which design structure is inherently safer than another.

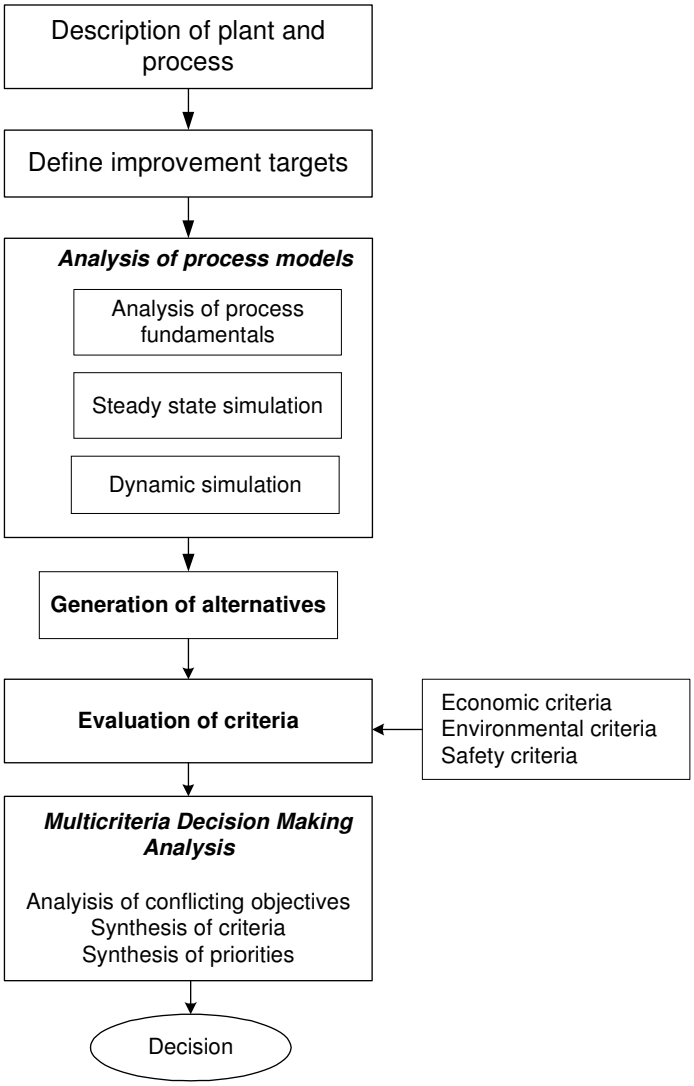


Figure 5-1. Systematic method for multicriteria analysis

The evaluation of each criterion will be described in the next section. Further, the decision making procedure based on analytical hierarchy process (AHP) framework is presented. The AHP method [115] is commonly used in order to support selection of the most promising design alternatives. The procedure is explained in chapter 4, namely synthesis of criteria, pairwise comparison, and synthesis of priorities.

5.2. Selected topics

5.2.1. Plant and process description

The investigated steam stripping distillation unit separates acetone from waste water. This unit is a part of hydrocarbon recovery unit [23]. The plant flow sheet for this research case study is shown in figure 5-2.

Table 5-1 shows the streams employed in the base design case. The concentrations of more volatile components are increased in the rectifying section of the column, while in the stripping section of the column, volatile components have progressively lower concentration.

The column has 35 valve trays. The feed stream is fed at tray 19 while live steam is injected into the base. Temperature at stage 9 is controlled by manipulating steam flowrate. The reflux is transferred under flow control back into the column on stage 1. The distillate (crude acetone) is pumped through to acetone recovery plant. The base product is discharged into the in-plant effluent pit.

Table 5-1. Streams data for the investigated column

Streams	**Flow rate [kg/hr]**
Feed	4020
Head	1802
Base	2821
Steam	603

Table 5-2. Component data of the investigated column included in ASPEN Plus simulation

Component	**CAS**	**Mass fraction [%]**
Methanol	67-56-1	0.0165
Acetaldehyde	75-07-0	0.0221
Methyl format	107-31-3	0.0377
Ethanol	64-17-5	0.0106
Acetone	67-64-1	0.1311
Methyl acetate	79-20-9	0.0234
Methyl ethyl ketone	78-93-3	0.0057
Ethyl acetate	141-78-6	0.0024
Diethyl ketone	96-22-0	0.0009
Water	7732-18-5	0.7268
Acetic acid	64-19-7	0.0175
Formic acid	64-18-6	0.0037
Propionic acid	79-09-4	0.0013

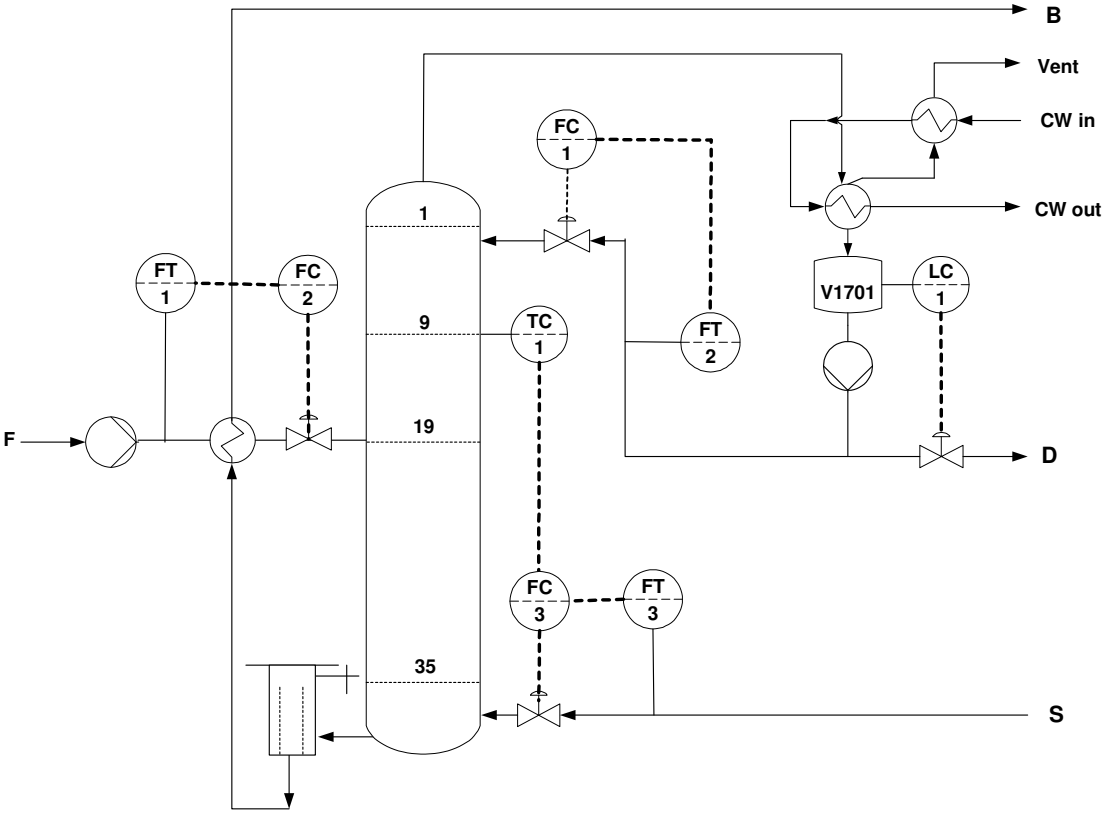


Figure 5-2. Base case of distillation unit under study. FC: Feed controller, LC: Level controller, TC: temperature controller, PC: pressure controller

5.2.2. Definition of improvement target

The problem statement of this work can be formulated as:

"Develop an improvement of acetone recovery plant by process design alternatives that effectively control plant performance, minimise waste and maintain plant safety".

The complete equality and inequality constraints are formulated as follows:

Equality constraints related to design limitation:

Subject to	:	N = 35 (Number of trays) D = 2 m (diameter of the column)

Inequality constraints related to component specification:

Distillate product	:	water < 10% (w/w) acetone > 50 % (w/w)
Base product	:	acetone < 2 % (w/w) methanol < 2 % (w/w) acidity < 3 % (w/w)

5.2.3. Generation of alternatives

Since the improvement task of an existing distillation process is a tedious iterative process including generation of some alternatives and a reasonable comparison of those different alternatives, then this section will address the potential design alternatives to meet the improvement target. Then, the exploration of possible design alternatives to achieve optimum design and operating condition of distillation unit is discussed in this section. The focus on process improvement (e.g. changing the process of the existing process with another process) is beyond the intention of this thesis work. However, the process improvement work will be illustrated briefly at the end of this section.

5.2.3.1. Alternatives for the improvement on design and operation

First, the improvement will take into consideration any structural and operation designs. This design and operation improvement steps deal with finding the alternative for distillation design under investigation that is likely to give rise to the desired quantity of acetone recovery.

In this case study, however, the design improvement will not consider the use of process alternatives or complex column using entrainer and fully thermally coupled columns as the possibility of heat integration to minimise energy consumption. While the single column is less expensive, it is also harder to control complex column containing two or more distillation units and therefore carries the risk of becoming operation problems. Instead of this, the sidestream design has been considered.

For each alternative plant, operability is studied to find optimum value of design variables. As a major component of process design, the key aspect of operability improvement is assessing the appropriate choice of controlled and manipulated variables.

Since the process in the case study exploits the formation of some azeotropes (as will be explained in the next section), then process modification may be efficient. As explained by Barnicki and Fair [13], physical solvents/entrainer (PSE) processes like azeotropic/ extractive distillation, liquid-liquid extraction and pervaporation may be more attractive than the standard distillation.

5.2.3.2. Alternatives considered in this case study

In this case study, sidestream distillation will be considered as the alternative for design improvement. The procedure for adding sidestream from the base case distillation design as well the requirements to perform the feasibility study in sidestream distillation design will refer to Alatiqi and Luyben, [3], Elaahi and Luyben [48] as well as Glinos. and Malone [53]. Figure 5-3 below represents the alternative for the improvement of design and operation.

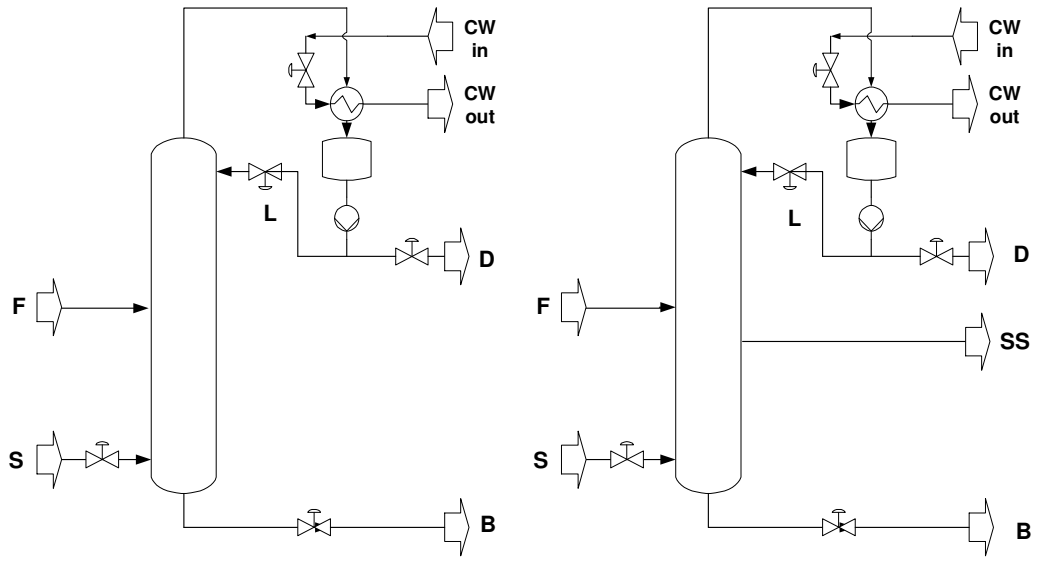


Figure 5-3. Alternatives analysed in the case study.

The control structure design uses the inferential control which involve temperature controller. For the study on dynamic simulation and the effects associated with disturbances, the following pairings of controlled variables (CV) and manipulated variables (MV) will be selected:

For base case design :

$$y = [p, H_{cond}, H_{base}, T_{rect}, T_{strip}]^T$$

$$u = [F_{CW}, D, B, L, F_S]^T$$

For sidestream design:

$$y = [p, H_{cond}, H_{base}, T_{rect}, T_{strip}, F_F]^T$$

$$u = [F_{CW}, D, B, L, F_S, F_{SS}]^T$$

where u and y is manipulated and controlled variable, respectively. F, H,T and p represent mass flowrate (kg/hr), high/level (m), temperature and pressure, respectively.

5.2.3.3. Alternatives proposed for process improvement

The scope of improvement can be extended to upstream processes. Figure 5-4 shows a part of hydrocarbon recovery plant. The aqueous return from acetone recovery plant is fed together with light pressure (LP) steam condensate to the distillation unit under study. Improvement proposal is installation of a decanter. This is based on liquid-liquid equilibrium study presented in section 5.3.2.2. The noncondensable and nonadsorbable gaseous hydrocarbon leave the process and are burnt in the Thermox plant to generate steam. The wateric-phase from decanter is continuously fed to the investigated distillation unit. The organic phase is recycled.

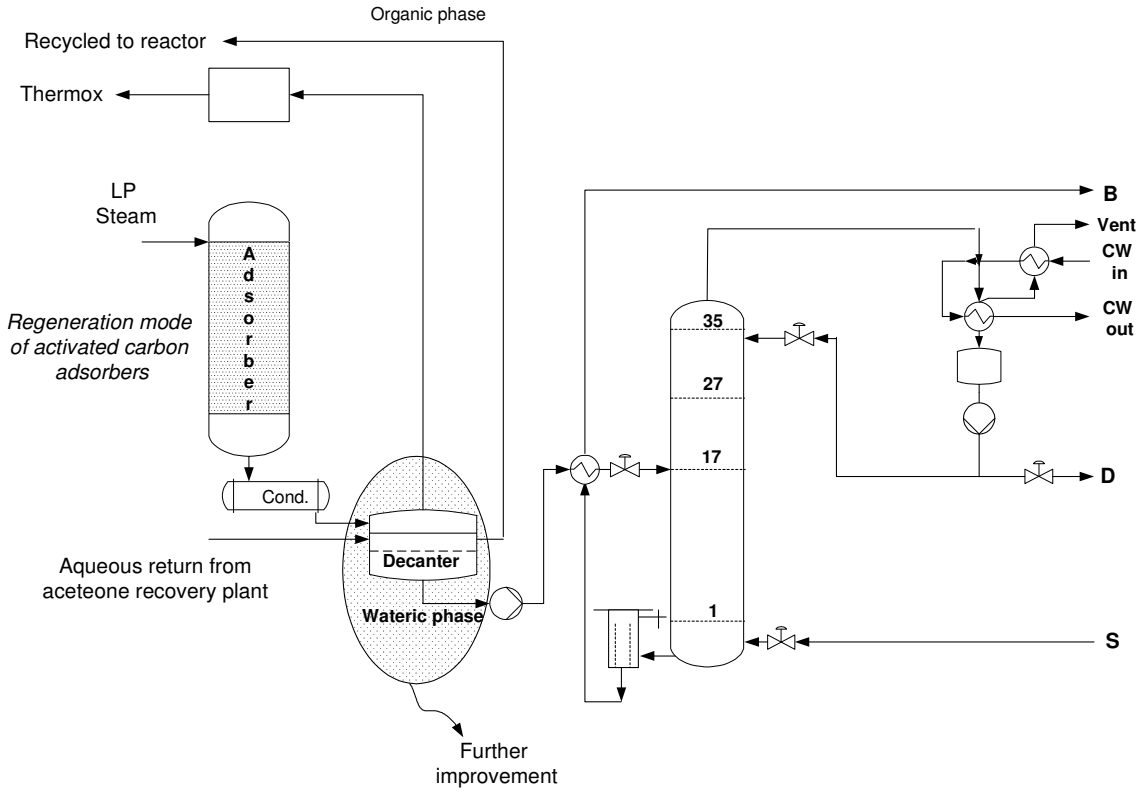


Figure 5-4. Extended view for further process improvement. The decantation process requires an analysis of liquid-liquid equilibrium

5.2.4. Discussion of criteria used

The main focus in this section is establishing criteria for improvement tasks according to definite improvement target as stated in section 5.2.2. The criteria definition shall consider all principles in designing and operating distillation column to operate properly, safely and environmentally friendly. Amongst of those criteria are:

- economic
- environmental
- safety

The first criteria requires decision maker to assess the economic viability of the investigated design. The criteria for economically feasible design in this existing plant will be based on total operating cost. Next, such design also should minimise potential environmental impact associated with waste component release from distillation design into the environment. In addition, to guarantee that the investigated plant is operating under viable and secure operation, the decision will include safety criteria as well. This safety criteria evaluation will consider inherent safety aspects of the plant and risk assessment.

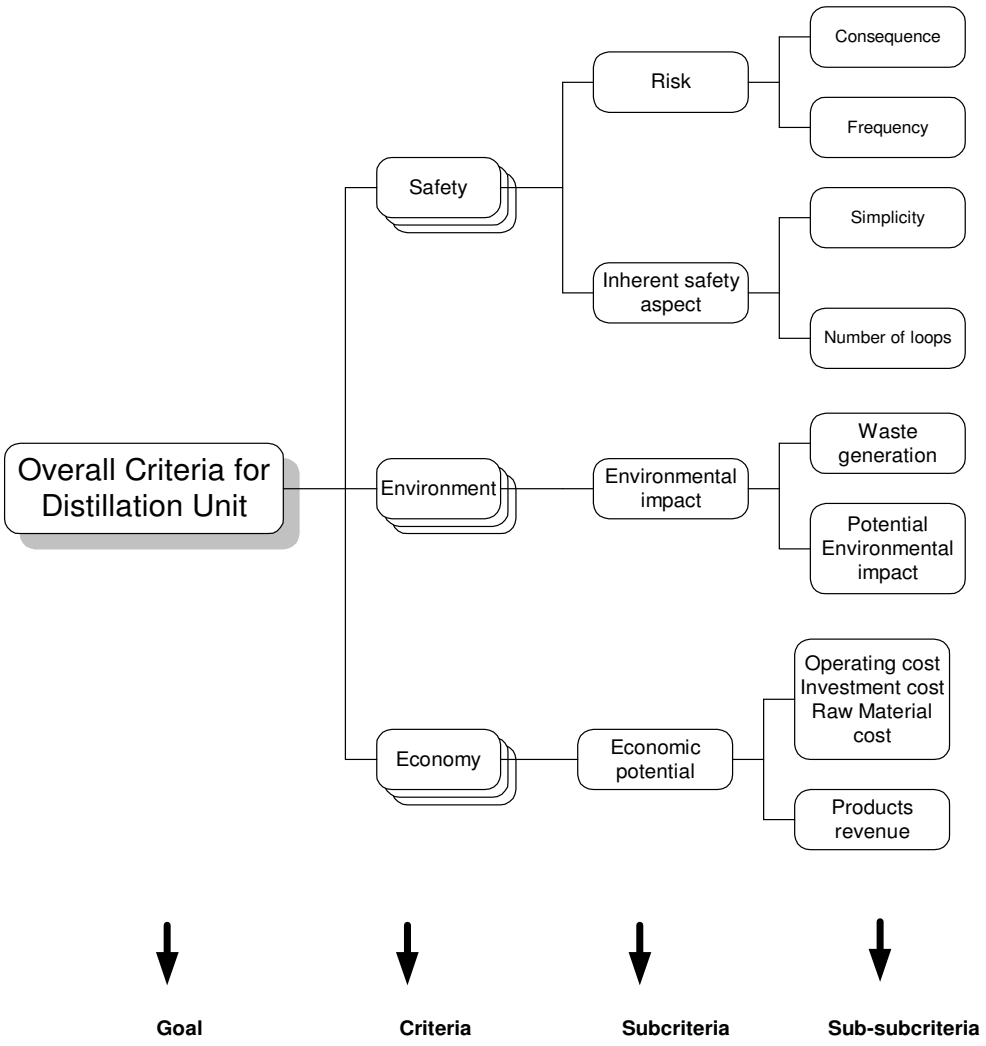


Figure 5-5. Criteria tree for multicriteria decision making in distillation unit

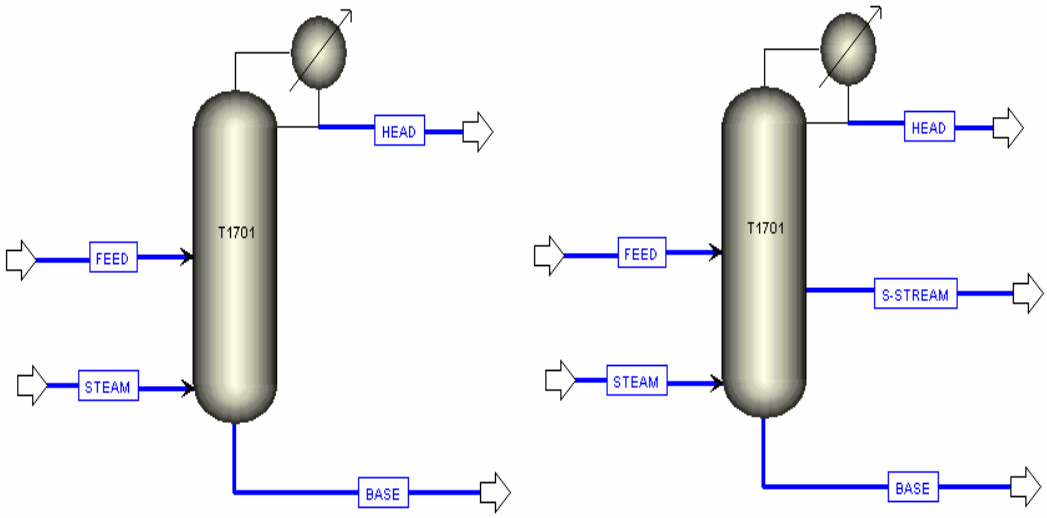
From the description above, the criteria tree for the development of multicriteria decision making in distillation unit is developed and shown in figure 5-5. The overall criterion is to satisfy all criteria. The alternative which meets the overall criterion within this framework is defined as the optimum alternative. The overall criteria is divided as criteria, subcriteria and sub-subcriteria. According to figure 5-5, following formulation of each subcriteria is formulated as follows:

- *Risk = f(consequence, frequency)*
- *Inherent safety = f(simplicity(number of streams), control loops)*
- *Environmental impact = f(waste generation, PEI)*
- *Economic = f(products flowrate, waste flowrate, operating cost)*

5.3. Definition and Analysis of process model and simulation basis

5.3.1. ASPEN Plus model

In this section, the simulation model used for the case study is described. The simulation results are expected to be representative for the actual plant operating. Figure 5-6 shows ASPEN Plus model developed for this case study.



(a). Base case design (b) Sidestream design

Figure 5-6. ASPEN Plus design developed for the case study

5.3.1.1. The ASPEN Plus setup and validation

The setup of the development of ASPEN Plus simulation is based on:

- Experimental vapour – liquid and liquid – liquid equilibrium (VLE/LLE) data as well as thermodynamic model reviewed binary interaction parameters.
- "Real dimension" of plant equipment that matches with the existing plant
- Actual operating condition of the existing plant
- Modified plant construction
- Simplified thermodynamic system (without including inert gases)

The investigated column is modelled with the "RadFrac" unit operation model that is suitable to deal with all types of multistage vapour-liquid fractionation operations. This includes also live steam stripping with a non-ideal liquid phase. The "strongly non-ideal liquid" is chosen for convergence method since the system is a non-ideal multi- component mixture. The input for component composition data as tabulated in table 5-2 are taken from the Analytical Services Laboratory (ASL) at

plant site (BTU – Report, 2002). The inert gases, however, have not been included in the model.

5.3.1.2. Special feature in ASPEN Plus

The process is simulated using ASPEN Plus for steady state design and ASPEN dynamic for dynamic simulation. Parameters that affect only the dynamic responses of the columns (such as column diameter, condenser vessel holdup and base holdup) are not needed in the steady state design, whereas those parameters must be specified in dynamic simulation. The tray-sizing tool in ASPEN plus is used to define the column diameters. The "RadFrac" column model is chosen for the process model and it numbers stages from the top down, starting with the condenser.

The flowsheet variables that are to be varied or held constant can be identified by using the "Design Spec-Vary" in ASPEN Plus. With the aid of ASPEN Plus, only block input and process feed stream variables may be varied. Once a variable with units has been selected, these units are displayed on this sheet. This form is also possible to specify values, or a range of values, for the varied variables. The steady-state simulation work is addressed to estimate the effects of available streams sensitivity into environmental impact and economic viability.

The calculation of cooling water flowrate is based on the calculation of heat which has to be removed in order to condensate the head stream. The calculation is based on the latent heat of vaporisation Δh_V of the mixture.

$$\Delta h_{V,mixture} = \sum_i \Delta h_{V,i} \cdot x_i \qquad (5\text{-}1)$$

The required cooling water flow rate is calculated by equations 5-3 and 5-4.

$$\dot{H} = \dot{M}_{G,head} \cdot \Delta h_{V,mixture} \qquad (5\text{-}2)$$

$$\dot{M}_{CW} = \frac{\dot{H}}{c_{P,CW} \cdot \left(T_{CW,out} - T_{CW,in}\right)} \qquad (5\text{-}3)$$

The cooling water temperature difference ΔT_{CW} is fixed to 5K as it is considered on the process data sheet, and $c_{P,CW}$ = 4.183 kJ/(kg · K).

5.3.2. Fundamentals of process

5.3.2.1. Analysis of process azeotropes

The presence of some azeotropes in the components mixture of the system under study presents the limit for the products compositions achievable in the column. Even though the analysis of azeotrope mixture is not the focus in this thesis, however, it is important to demonstrate that the formation of azeotrope mixtures should be understood as the limitation of the separation process to attain its higher product

purity. Table 5-3 shows some azeotrope systems in the system under study. The information containing in the types of components included for separation is supposed to provide some understanding of the important concepts and aspects of the systems under study.

Thus, the discussion in this section follows the standard analysis methodology discussed in many text books and references such as Luyben [101], Stichlmair [128] and Doherty [40]. First, the complexity of the phase is illustrated by displaying selected binary and ternary systems. The binary systems methanol – acetone, methanol – methyl acetate and acetone – methyl acetate as well as ternary system of acetone - methyl acetate – methanol are selected. The experimental vapour – liquid equilibrium data for this system as well as thermodynamic parameters are taken from DECHEMA data book [55],[56]. Figure 5-7 shows three binary diagrams and one ternary diagram of the selected components. The diagrams in figure 5-7 show the existence of binary and ternary azeotropes. Because of this azeotropic formation, distillation technique can not achieve high purity products.

Table 5-3. Some binary azeotrope mixtures in the investigated system, according to Barnicki and Fair [13] and Gmehling [55],[56]

No	Binary of ternary systems	Boiling points [°C], 1 atm	Composition
1	Water – formic acid	107.65	22 % water
2	Methanol - acetone	55.5	12% methanol
3	Methanol – methyl ethyl ketone	63.5	70 % methanol
4	Ethanol – methyl ethyl ketone	74.0	39 % ethanol
5	Water – methyl ethyl ketone	73.4	11.3 % water
6	Acetone – methyl acetate	78.17	4 % acetone
7	Methanol – methyl acetate	55.7	55.3 % methanol
8	Methanol – methyl acetate	53.8	35% methanol

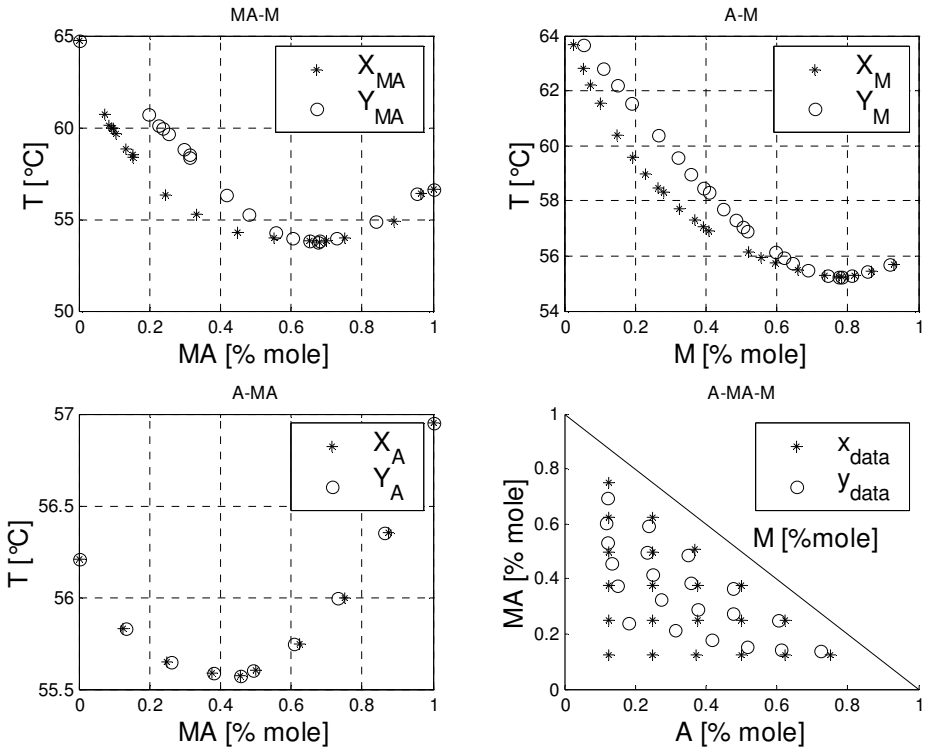


Figure 5-7**.** Binary and ternary diagrams of acetone (A)– methyl acetate (MA) – methanol (M) system. Data are taken from Gmehling[55],[56].

Three binary azeotropes methyl of acetate – methanol (MA-M), acetone – methanol (A-M), acetone – methyl acetate (A-MA) and one ternary azeotrope of acetone – methyl acetate –methanol (A-MA-M) exist in the ternary system of acetone – methyl acetate – methanol system showing azeotropic mixtures of the system and limiting the system in attaining high purity products.

5.3.2.2. Thermodynamic model

In the simulation of the investigated distillation unit, the phase equilibrium calculation is tightly coupled with the interstage material and energy balances, and efficient procedures for simulation of multistage units are therefore based on simultaneous solution of the material and energy balances and the equilibrium relations. Accurate vapour liquid equilibrium (VLE) data is therefore a cornerstone of reliable process simulation of the investigated case study. Accordingly, a proper selection of thermodynamic models during process simulation is absolutely necessary as a starting point for accurate results of process simulation. In this case study, the selection for selecting NRTL models follows the decision tree according to Carlson [27], as shown in figure 2-1.

Process simulators like ASPEN Plus requires user to select thermodynamic model to be used. However, very often the user does not have the knowledge and experience to choose wisely among the options. The selection is often based on familiarity, hearsay or accessibility. When the chosen thermodynamic model does not

represent correct phase behaviour, distillation calculation will be wrong. Historically, Kister [83],[84] reported that there have been about 20 % of distillation malfunction cases resulting from deviation or mishaps between simulation results and real condition of phase behaviour.

The following section explains the procedure to improve the simulation results of thermodynamic phase equilibrium in distillation column. The basis for the proposed procedure is the availability of some form of data (LLE, VLE, or actual plant/design operating data) against which the predicted results can be verified by the estimation/ adjustment of the model parameters (e.g. the group interaction parameters for the UNIFAC method).

Examples of similar effort in the past are those of Alcantara, Westerberg and Rychener [16] who have developed an expert system for selection of appropriate vapour-liquid equilibrium methods to use in process engineering calculation; and Gani [52] who has developed a knowledge based system for the selection of thermodynamic models using the set of indices selection. The present work gives an alternative methodology which is more applicable in recent situation using process simulator.

The Aspen Plus manual regression method according to figure 5-8 is performed using experimental data from DECHEMA data sets and from plant documentation. The term automatic regression in this paper was used to describe estimation of NRTL BIP's (Binary interaction parameters) using selected thermodynamic method (i.e. UNIFAC, UNIFAC (Do), etc) as the base method. The advantage of automatic regression is that it needs less time than manual regression when attempts being made to obtain reliable phase equilibrium data.

Another attempt to improve the prediction of phase equilibria is through including some simulation results from VLE estimation for NRTL BIPs regression. This is called in this thesis as "manual regression". The intention in both procedures (automatic and manual regression) is to improve thermodynamic parameters. The important step in this procedure is parameter estimation by positive or negative perturbation (e.g. increasing or decreasing the values of parameters) until minimum residual values are obtained [142]:

$$residual = \sum_{i=1}^{NC} \sum_{j=1}^{NP} w_i \cdot \left(p_{i,j}^{c} - p_{i,j}^{d} \right)^2 \qquad (5\text{-}4)$$

where $p_{i,j}^{c}$ is the calculated of thermodynamic property of component i of set j, $p_{i,j}^{d}$ is the desired (or experimentally determined) thermodynamic property of component i of set j, and w_i is a weighting factor for component i whose value can vary from 0 to 1.

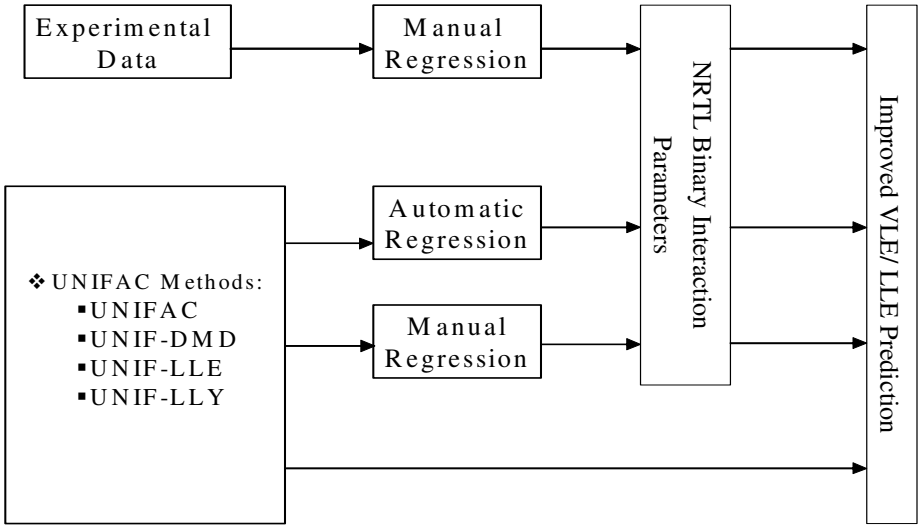


Figure 5-8. Automatic regression procedure to improve phase equilibrium behaviour

NRTL model parameters for the simulation of case study

The selection of thermodynamic model is aimed at answering key point that requires attentiveness for the validation of distillation simulations to obtain good VLE estimation and providing a comparison between simulation results and experimental data. The comparison of simulation results and experimental are supported by graphical techniques to indicate where deviations of simulation occur. The binary systems acetone-methanol, acetone – methyl acetate and methanol – methyl acetate are used for illustrating the selection of thermodynamic model and the use of relevant thermodynamic parameters for simulation of the investigated systems. The column is operating at atmospheric pressure. The experimental data are available in the literature [55],[56], the simulation was made using NRTL thermodynamic model and the results of vapour – liquid equilibria calculation were compared with the experimental data.

Figure 5-9 shows a good agreement between VLE simulation results and experimental data. It is obvious that for these binary systems, VLE simulation result are in good agreement with experimental data. Table 5-4 shows binary interaction parameters of NRTL model that are used in the simulation.

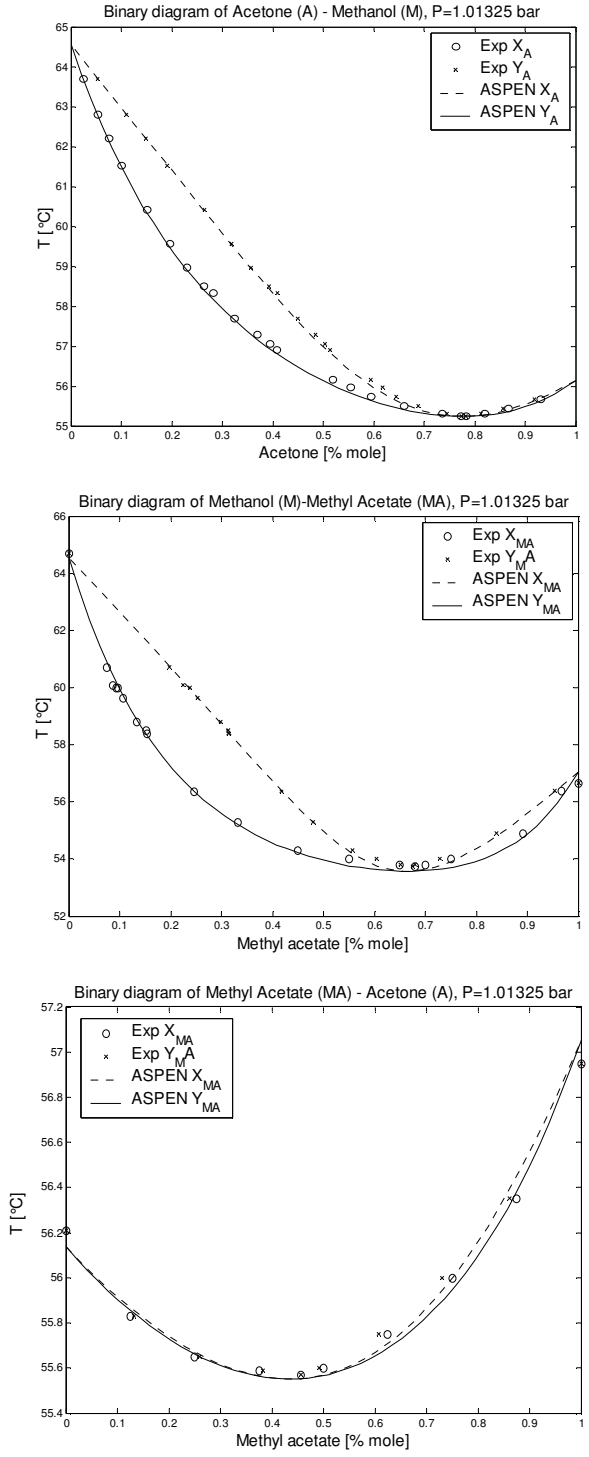


Figure 5-9**.** Comparison of experimental data (Exp) with aspen plus simulation (ASPEN) using NRTL thermodynamic model for three binary systems of acetone – methanol (above), methanol - methyl acetate (middle) and methyl acetate – acetone (below) at 1.01325 bar. Data are taken from Gmehling [55],[56]

Table 5-4. Thermodynamic parameters of the binary systems of acetone (A)- methyl acetate (MA) – methanol (M). Data are taken from Gmehling [55],[56]

NRTL parameters	Binary components of NRTL model		
	A(1) – MA(2)	**MA(1) – M(2)**	**M(1) – A(2)**
A_{12}	360.0288	108.6972	214.2632
A_{21}	-237.7587	575.2739	194.2969
α	0.3064	0.2968	0.3008
B_{12}	-	2.75	1.79
B_{21}	-	2.32	1.82

Adjustment of NRTL model parameters

When the VLE simulation differs from experimental data, thermodynamic parameters must be adjusted trough regression method in ASPEN plus. As an example, the binary systems acetone – ethyl acetate, acetone – ethanol and ethanol – ethyl acetate are used. Experimental data are provided from previous research report [23]. The simulations were carried out and the results are compared with the experimental data.

Regression were made and the results are shown in the figure 5-10. It can be easily seen that the best simulation results are obtained by adjusting the parameters by proposed procedure. The VLE prediction after and before adjustment of thermodynamic parameters together with experimental data are compared. The simulation results generated from adjustment gives a good agreement with the experimental data.

Table 5-5. Thermodynamic parameters of the binary components of ethanol acetone (A)- ethyl acetate (EA) – ethanol (E). Data are from courtesy of BP [23]

NRTL parameters	Binary components		
	E(1) – A(2)	**E(1) – EA(2)**	**A(1) – EA(2)**
A_{12}	0.0	0.0	0.0
A_{21}	0.0	0.0	0.0
α	0.3	0.3	0.3
B_{12}	153.59561	106.76002	160.72
B_{21}	63.598694	209.6136	-92.9

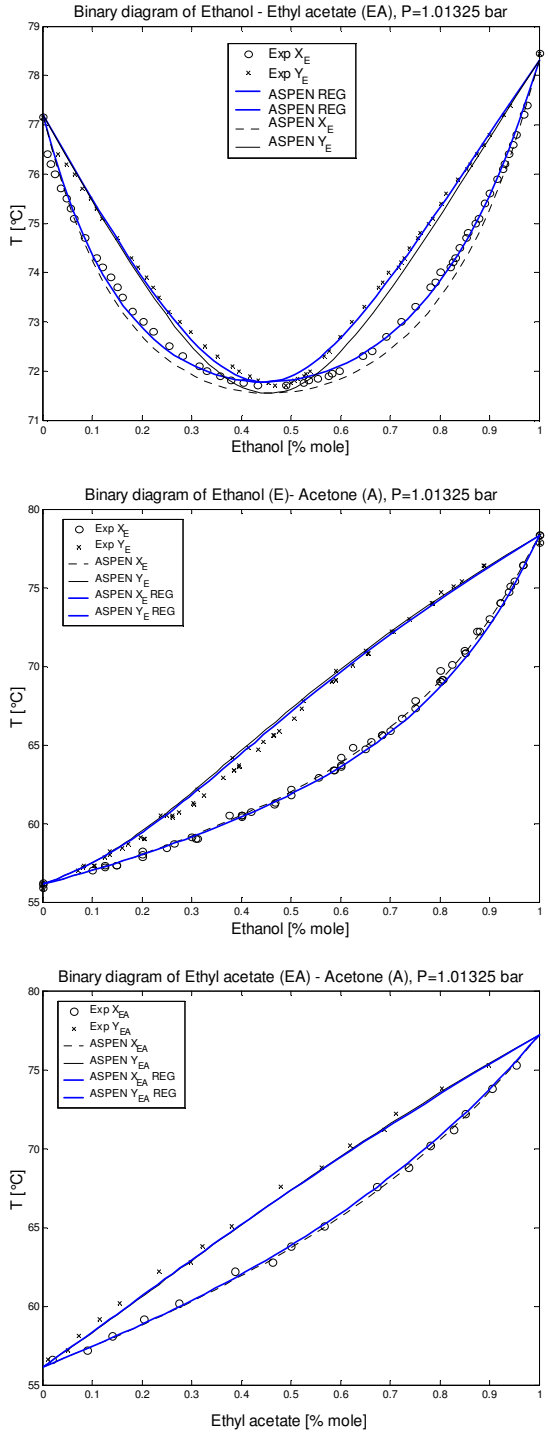


Figure 5-10**.** Comparison of experimental data (Exp), aspen plus simulation (ASPEN) and aspen plus simulation (ASPEN REG) using NRTL thermodynamic model for three binary systems of acetone – ethanol (above), ethanol - ethyl acetate (middle) and ethyl acetate – acetone (below) at 1.01325 bar. Data are courtesy from BP company

User model parameters in ASPEN Plus

The regressed NRTL-paramters are offered in the NRTL – BIPs data sheet in ASPEN Plus and can be selected for the further simulation. All thermodynamic parameters are inserted into NRTL parameters as "user input data" in simulation of the investigated case study. Figure 5-11 shows the illustration of the application of proposed procedure in providing thermodynamic parameters into user input data in aspen plus simulation.

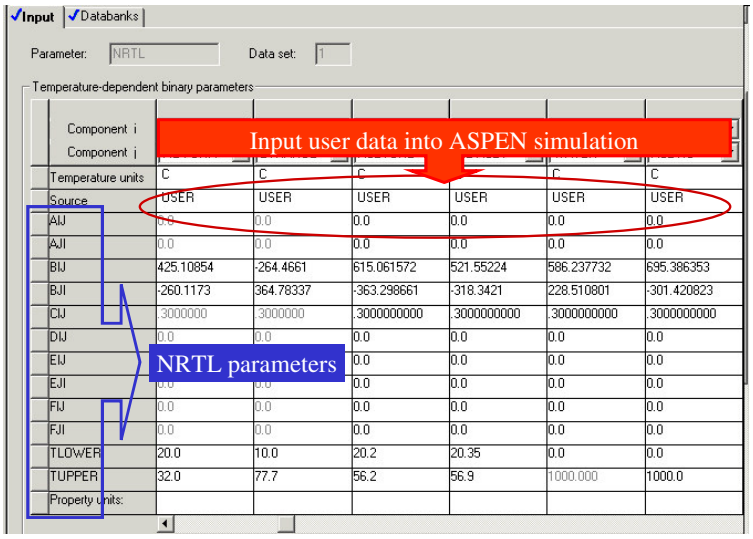


Figure 5-11. Application of the procedure for input user data in ASPEN plus for binary interaction parameters

Parameters regression for liquid - liquid equilibrium systems

The applied procedure can also be used for liquid-liquid equilibrium systems. According to the explanation in section 5.2.3.3, the use this procedure of liquid-liquid equilibrium will play important role for decantation system in upstream treatment. As an example, a ternary system benzene – water – formic acid is used. Figure 5-12 shows a curvature comparison between experimental data and Aspen plus simulation results. The figure below shows discrepancies between experimental data and ASPEN Plus simulation results. The observed results imply that it is necessary to validate phase equilibrium prediction when using Aspen plus inherent BIPs. This result therefore serves as motivation in determining the appropriate thermodynamic parameters for liquid-liquid equilibrium system in ASPEN Plus.

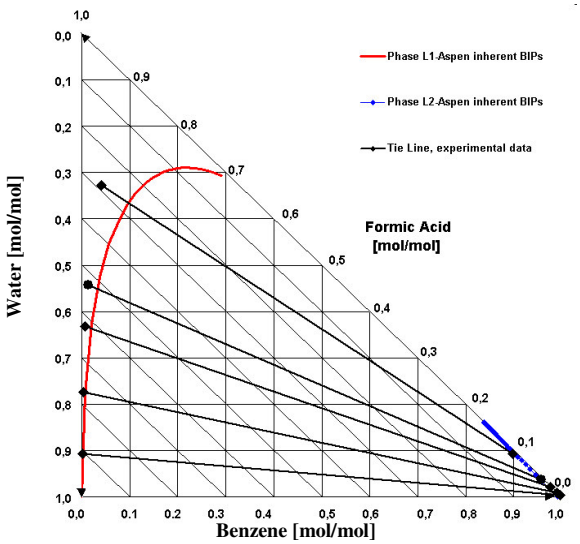


Figure 5-12. The discrepancy between ASPEN Plus inherent BIPs and experimental data for ternary system of benzene – formic acid – water

A good agreement between the experimental and predicted data from automatic regression of NRTL BIP's using experimental data was observed. Figures 5-13 and 5-14 show a comparison between VLE estimation from ASPEN Plus regression with experimental data for ternary system benzene – water – formic acid (figure 5-13) and binary subsystems benzene-water and benzene – formic acid (figure 5-14). The regression parameters of the system are tabulated in table 5-6.

Table 5-6. Thermodynamic parameters of the binary components of water (W), formic acid (FA) and benzene (B)

NRTL parameters	**Binary components of NRTL model**		
	B(1) – FA(2) *)	**W(1) – B(2)** *)	**W(1) – FA(2)** **)
A_{12}	-54.593	140.0847	-2.5864
A_{21}	213.3302	45.1905	4.5156
α	0.2	0.2	0.3
B_{12}	3064.3235	-5954.3071	725-0173
B_{21}	-9059.4697	591.3676	-1432.0835

Note: The sign of **) and :*) denote that the system completely miscible binary subsystems and partly immiscible binary subsystems, respectively.

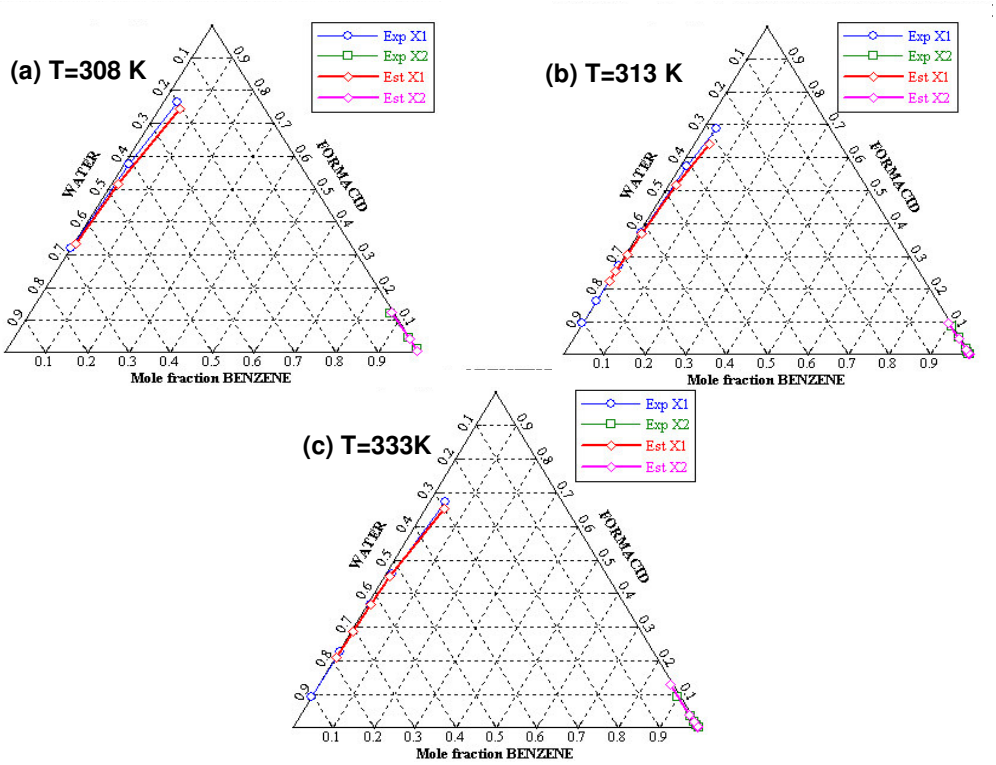


Figure 5-13. Benzene – water - formic acid at temperatures of (a-c, in K) 308, 313, 333 respectively

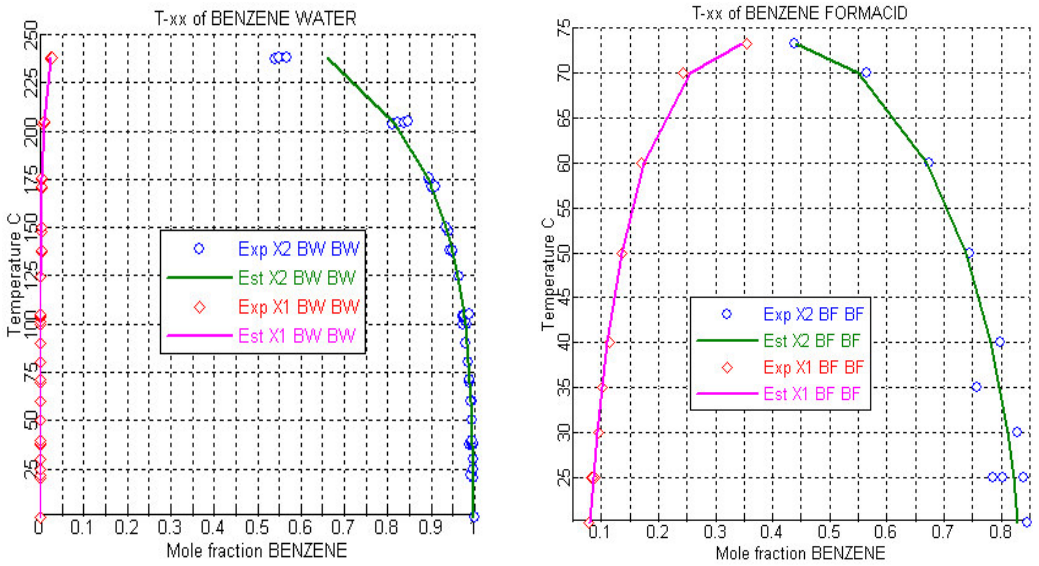


Figure 5-14. Binary subsystems of benzene – water and benzene - formic acid

5.4. Steady state analysis

The steady state simulation in this thesis should give an insight how well a given control structure will perform. Following work will intend to find a sensitive controlled variable so that the occurrence of even small disturbance is detected and compensated through appropriate control action.

5.4.1. Streams relationships

For proper design and control of the investigated design, the overall models that describe the effect of the input (flows) and outputs (product composition) should be understood. Therefore, the steady state input-output relationship has to be studied.

First, the discussion will cover the relevance concerning some common feasibility study based on an attainment of component purification in the product streams (distillate and bottom streams). In this context, it is important to note that an accurate targeting of the economic criteria is only guaranteed if the set of product and non-product stream specifications is feasible (i.e. it obeys the limitations established by decision maker).

Since the extent of components released in distillation unit relies on vapour and liquid equilibrium at each tray, then the correlation of those components fraction can be formulated as

$$[\ x_{n+1}, y_{n+1}, T_{n+1}, V_{n+1}, L_n\ ] = f\left[x_n, D, x_D, h_D, p, \dot{Q}_{CON} \right] \tag{5-5}$$

Examination of equation above shows that for a fixed product specification D, x_D, h_D and a fixed pressure p the course of the profile starting at the product composition only depends on the condenser heat duty $\dot{Q}_{CON}$ which depends on reflux. The profile of the stripping section can be formulated analogously as a function of the steam heat duty $\dot{Q}_S$. Both heat duties are connected by the energy balance around the columns

$$\dot{Q}_S + F_F \cdot h_F = D \cdot h_D + B \cdot h_B - F_F \cdot h_F + \dot{Q}_{CON} \tag{5-6}$$

where the steam heat duty, in the case of direct steam, is a function of steam flowrate, F_S and steam enthalpy h_S

$$\dot{Q}_S = F_S \cdot h_S \tag{5-7}$$

Hence the equation becomes:

$$F_S \cdot h_S + F_F \cdot h_F = D \cdot h_D + B \cdot h_B - F_F \cdot h_F + \dot{Q}_{CON} \tag{5-8}$$

Analogously, component mass balance on the tray can be formulated as:

$$\frac{d}{dt}\left(M_N^{tot} \cdot x_{i,N}\right) = L_{N+1} \cdot x_{i,N+1} + V_{N-1} \cdot y_{i,N-1} - L_N \cdot x_{i,N} - V_N \cdot y_{i,N} \quad (5\text{-}9)$$

where

$$(x_{i,N+1}, x_{i,N-1}, y_N, y_{N-1}) = f(p,T) \quad (5\text{-}10)$$

Therefore, the column profiles depend mainly only on parameters like condenser duty, steam flowrate F_S and/or reflux ratio r and compositions in distillate and bottom products.

Figure 5-15 shows a profile of component mass fractions along the tray. According to their boiling points, the components included in the system are categorized into low boiling components (LBC), middle boiling components (MBC) and heavy boiling components (HBC). The desired product, acetone, is withdrawn with the distillate stream while acids and water are withdrawn with bottom stream. MBC is distributed in the top and bottom section of the column but with the highest concentration in the middle section of the column. The phenomena where majority of MBC is located in the middle section of distillation called as trapped column [27]. The higher 'trapped components' contained in distillation unit, the higher risk due to flooding. Adding sidestream is one of the solution to solve such potential malfunction where more MBC's will flow through sidestream from middle section of distillation unit.

The profile of component mass fraction of the sidestream alternative is depicted in the second row of the figure 5-15 below. Figure 5-15 also tells that sidestream design will result in lower "trapped component" of MBC and improve acetone concentration in the distillate stream.

In order to develop a sidestream distillation as design alternative, a decision should be made to choose sidestream location. Since the objective of this sidestream installation is to withdraw some middle boiling components, therefore the decision should be based on the location that gives maximum middle boiling components in sidestream flowrate. From figure 5-16 shows that sidestream location should be designed between the tray 20 – 23 in order to maximise methanol fraction in sidestream. Figure 5-16 shows that methanol composition in sidestream will be higher starting from sidestream location on the tray 20 and decrease after tray 23. For this reason, tray 20 is chosen for sidestream location.

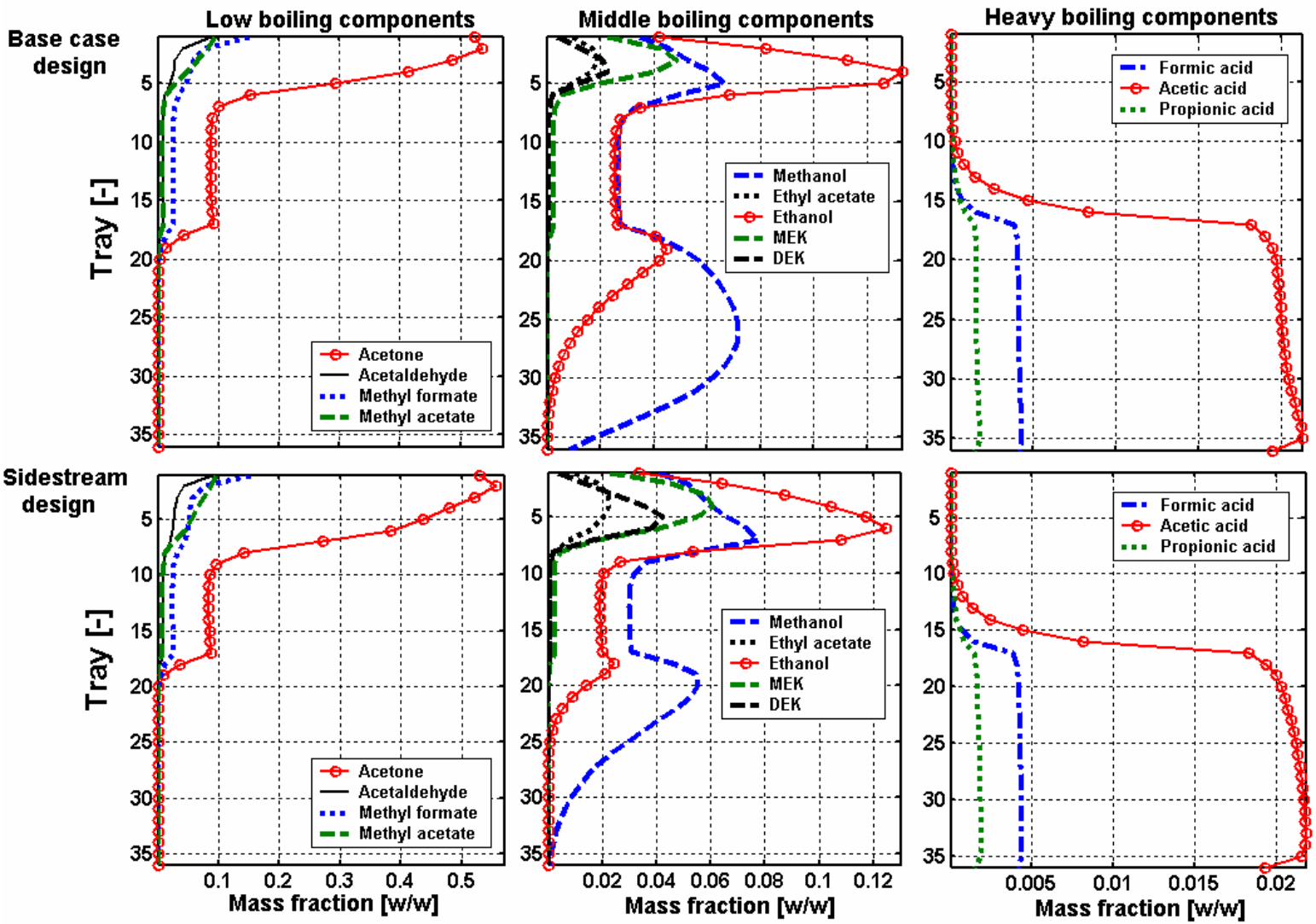


Figure 5-15. Profile of components mass fraction for base case distillation design (first row) and sidestream distillation design (second row). Feed flowrate is 4020 kg/hr. Sidestream flowrate is 450 kg/hr (for sidestream design).

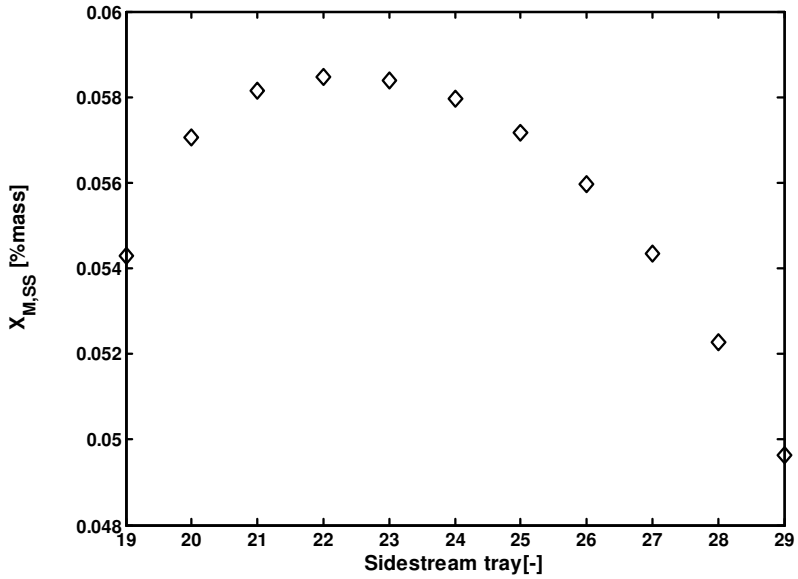


Figure 5-16. Selection of sidestream location based on the maximum methanol withdrawn. Sidestream and feed flowrates are 450 kg/hr and 4020 kg/hr respectively.

5.4.2. Location of temperature sensor

When choosing a temperature control location, a point where the temperature changes significantly over a few trays will be pointed out. Figure 5-17 represents temperature variation in representative tray with respect to steam and reflux flowrates. This tends to indicate a break in the composition profile of a component and means that the temperature will be sensitive to a manipulator (e.g. reflux or steam flowrates). According to figure 5-17 below, the sensitive tray with respect to temperature changes are tray 4 and tray 20 for base case design and tray 4 and 23 for sidestream design.

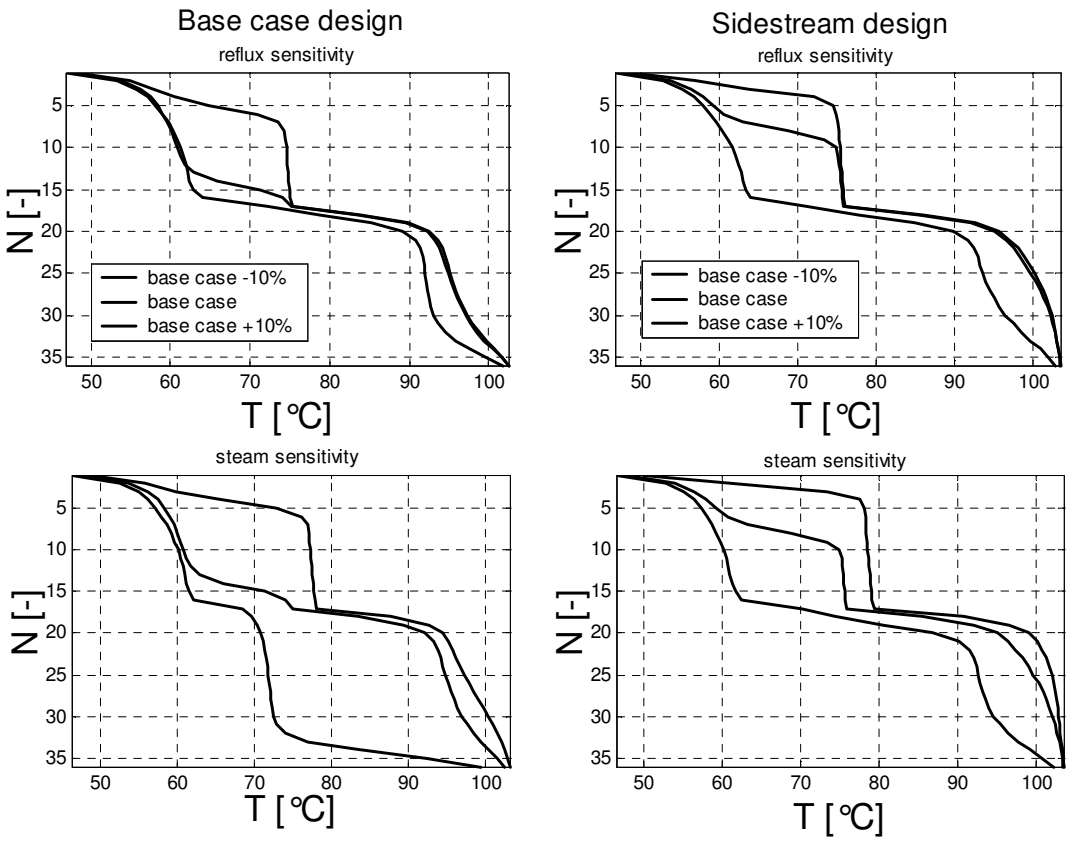


Figure 5-17. Steam and reflux sensitivities with respect to changes on trays temperatures for base case distillation design without sidestream (figures on the left) and with sidestream (figures on the right)

5.4.3. Concluding remarks on steady state simulation

This section presented stream relationship for the investigated distillation unit to provide a basis of mass and energy balances. Results from this section suggested that column with sidestream keeps better product quality and gives less environmental risk due to unseparated components in the base stream, compared to the existing column without sidestream. For this reason, therefore, sidestream column gives more attractive solution for waste minimisation objectives but not for inherently safer design objectives.

Another result of steady state simulation discussed in this section is a sensitivity analysis work to find optimum controller location for both design alternatives. The sensitivity is based on changes of trays temperature due to steam flowrates and reflux ratio changes.

This case study considers the use of dual temperature control. Therefore, a more advanced selection of optimum selection of tray location for temperature controller can follow a method called singular value decomposition (svd) [100]. This methodology can be applied for further study in this thesis.

5.5. Dynamic simulation

As the basic understanding of the dynamic behavior of the distillation unit, a dynamic simulation of distillation unit under investigation is required. Dynamic simulation in this section will investigate operability and control systems, look at modes of operation in various changes of setpoint and disturbances and study safety related questions. Thus, this dynamic simulation is expected to provide basic understanding to the cause of operational problems as the first step toward solving those problems as well as evaluating improvement possibilities.

As a comparison, some work on addressing safety assessment through dynamic simulation have been performed previously, those are Luyben [104] who has investigated disadvantage of inherently safer design from dynamic point of view, and Suhendra, Can, Compart and Witt [134] who have integrated and described the usage of dynamic simulation as a tool for assessing safety in distillation column. Now, the discussion in this section intends to use dynamic simulation to point out weak points in distillation unit operation due to some disturbances and set point changes, predict the consequences of operational failures and ensure that distillation column control is designed safely to handle such events. It means, the result on dynamic simulation should be the basic for assessing safety in both base case and sidestream design alternative. The discussion will be separated into two sections, the discussion regarding set point changes and the description of disturbances in the investigated unit, respectively.

Dynamic simulation is carried out using ASPEN Dynamic. Figure 5-19 and 5-20 show the ASPEN Dynamic process flowsheet with control configuration for base case and sidestream distillation designs, respectively. For base case distillation column, the column has five manipulated variables, namely cooling water, reflux, distillate, bottom, and steam flowrates. Thus, there are five degrees of freedom. There are two variables that need be controlled for stabilisation of the column, namely the condenser and bottom levels. This leaves the degree of freedom 3 for optimisation. The three degrees of freedom can be chosen as controlled variables are the pressure and two stage temperatures for quality control.

As shown in figure 5-20, the additional sidestream will add one degree of freedom for sidestream flowrate. The possible controlled variable is feed forward controller so that total degree of freedom will be six. Summary of controlled and manipulated variables is shown in table 5-7 and the values for each manipulated and controlled variables are tabulated in table 5-8.

The dynamic simulation is developed using flow driven simulation of ASPEN dynamics. The column pressure is controlled by manipulating cooling water flow rate using proportional-integral (PI) controller (K_c = 20) and λ_I = 12 min; default settings from ASPEN Dynamics). Reflux is manipulated to control column temperature on tray 2. Column base level is controlled by manipulating bottom flow using proportional controller (K_c = 2). Temperatures on tray 2 and 23 are selected for quality control of distillate and bottom product. The temperature controllers are PI and are tuned using the Tyreus-Luyben settings.

Table 5-7. Summary of controlled and manipulated variables for distillation system for base case and sidestream distillation units

Base case distillation unit			
No	**Controller**	**Controlled Variable**	**Manipulated Variable**
1	Pressure control	Pressure on stage 1	Cooling water flow rate
2	Condenser level controller	Liquid level on stage 1	Distillate flow rate
3	Reflux / head controller for distillate quality	Temperature at stage 2	Reflux flow rate
4	Steam/ bottom controller for bottom product quality	Temperature at stage 23	Steam flow rate
5	Sump level controller	Sump level	Bottom flow rate
Sidestream distillation unit			
No	**Controller**	**Controlled Variable**	**Manipulated Variable**
1	Pressure control	Pressure on stage 1	Cooling water flow rate
2	Condenser level controller	Liquid level on stage 1	Distillate flow rate
3	Reflux / head controller for distillate quality	Temperature at stage 2	Reflux flow rate
4	Steam/ bottom controller for bottom product quality	Temperature at stage 23	Steam flow rate
5	Sump level controller	Sump level	Bottom flow rate
6	Sidestream controller	Ratio of feed/sidestream flow rate	Sidestream flow rate

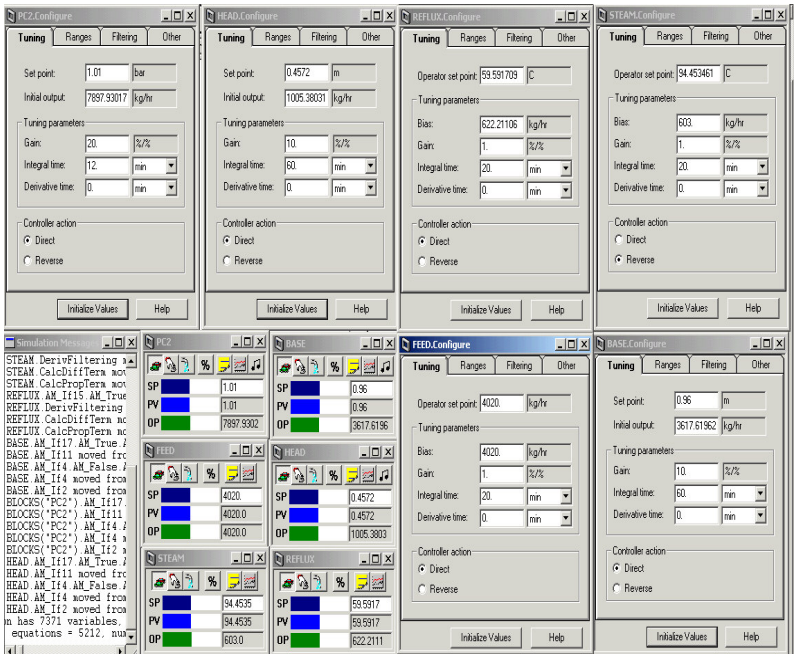


Figure 5-18. Controller configuration in ASPEN plus for base case distillation design

Table 5-8. Process variables at operation points

Base case design		Sidestream design	
Process variables	**Operation point**	**Process variables**	**Operation point**
Steam	603 kg/h	Steam	602 kg/h
Base stream	3618 kg/h	Base stream	3185 kg/h
Reflux	622 kg/h	Reflux	691 kg/h
Cooling water	7898 kg/h	Cooling water	8191 kg/h
Feed	4020 kg/h	Feed	4020 kg/h
Distillate stream	1005 kg/h	Distillate stream	987 kg/h
-	-	Sidestream	450 kg/h

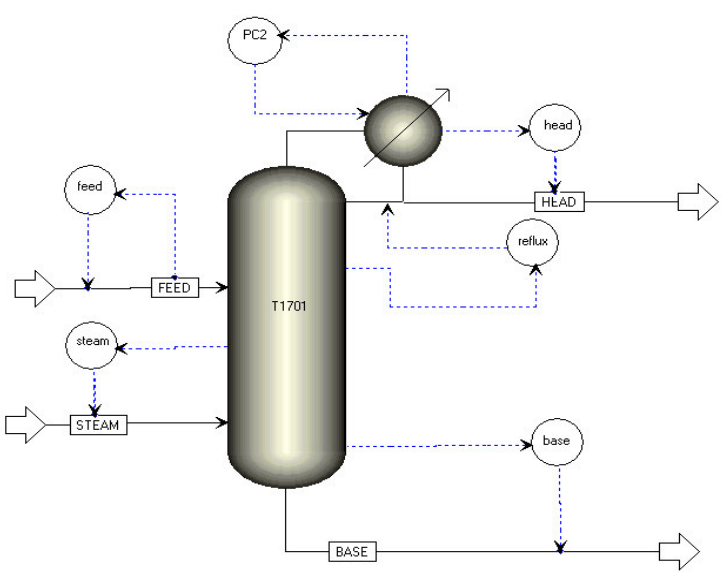


Figure 5-19. Control configuration for base case distillation unit

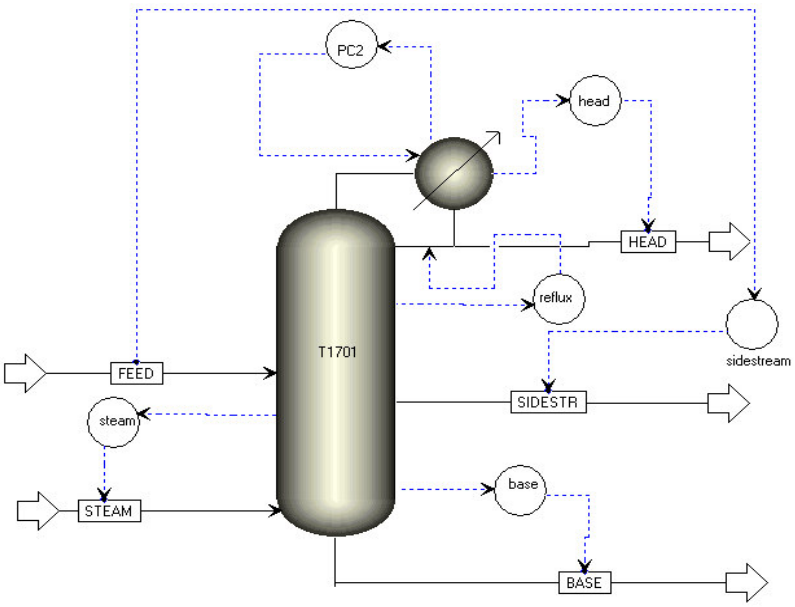


Figure 5-20. Control configuration for sidestream distillation unit

5.5.1. Set point in the control system

The dual temperature control is developed to maintain the target on product purities and impurities specification hence keeping the distillation products in high quality and environmentally friendly. The discussion in this section is regarding the effects of set point changes. The base design uses tray temperature controller on tray 4 and 20 whereas the sidestream design uses tray temperature controller on tray 4 and 23.

Figure 5-21 shows the effects of temperature set point changes of bottom (tray 20, right) and top section (tray 4, left) in the base case distillation design. Figure 5-21 shows that set point changes lead to reduction of acetone and water in distillate (figure 5-21B). Changes on temperature setpoint also affects the steam and reflux flowrates to the column, as shown in figures 5-21C to 5-21F. Both figures tell that as temperature setpoint on tray 4 is reduced by 10%, reflux and steam flowrates increase, and visa versa for temperature set point on tray 4 increases (figure 5-21C and 5-21E). Whereas, as temperature set point on tray 20 is decreased by 10%, reflux and steam flowrates increases, and visa versa (figure 5-21D and 5-21F). Figure 5-22 shows the effects of temperature set point change in sidestream design. The effects of temperature set point changes on all items (product purities, reflux and steam flowrate) are similar to the base case without sidestream. The only assumption is temperature at T_4–10%. In that case, composition profile for the base case is not as expected. Also, in some of the cases analysed (T_4 – 10% and T_{20} +10% and T_{23} + 10%) reflux stream reached predefined limit. These findings tell that the disturbance of 10 % temperature change was much too intensive.

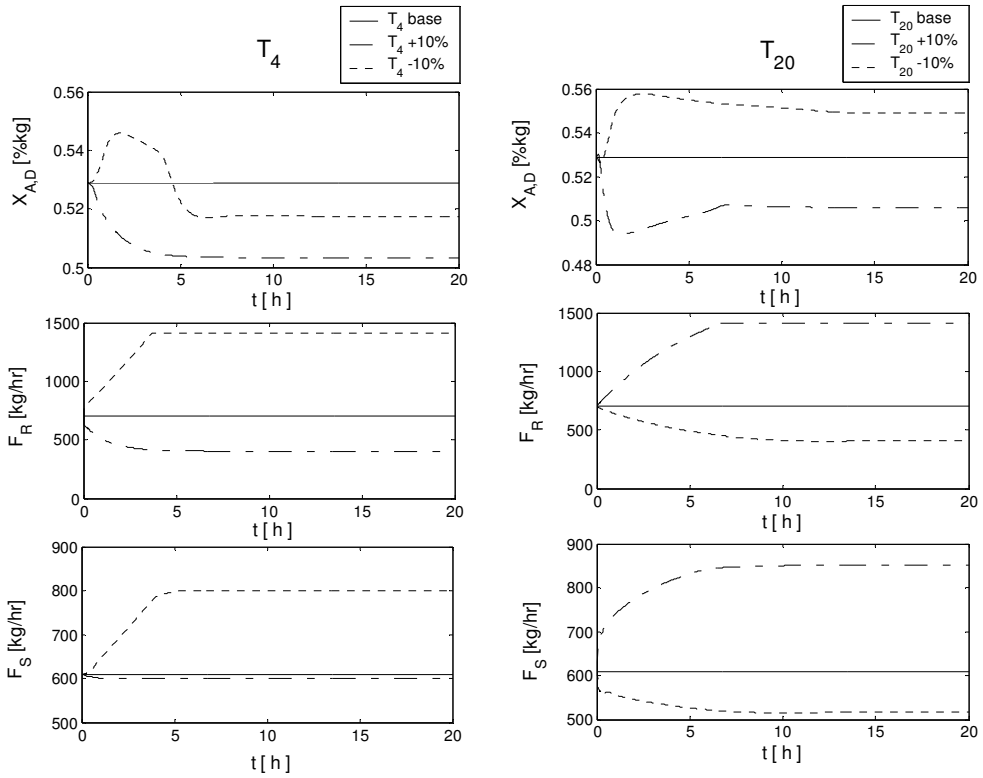


Figure 5-21. Effects of set point changes on acetone recovery as well as reflux and steam flowrates in the base case distillation design

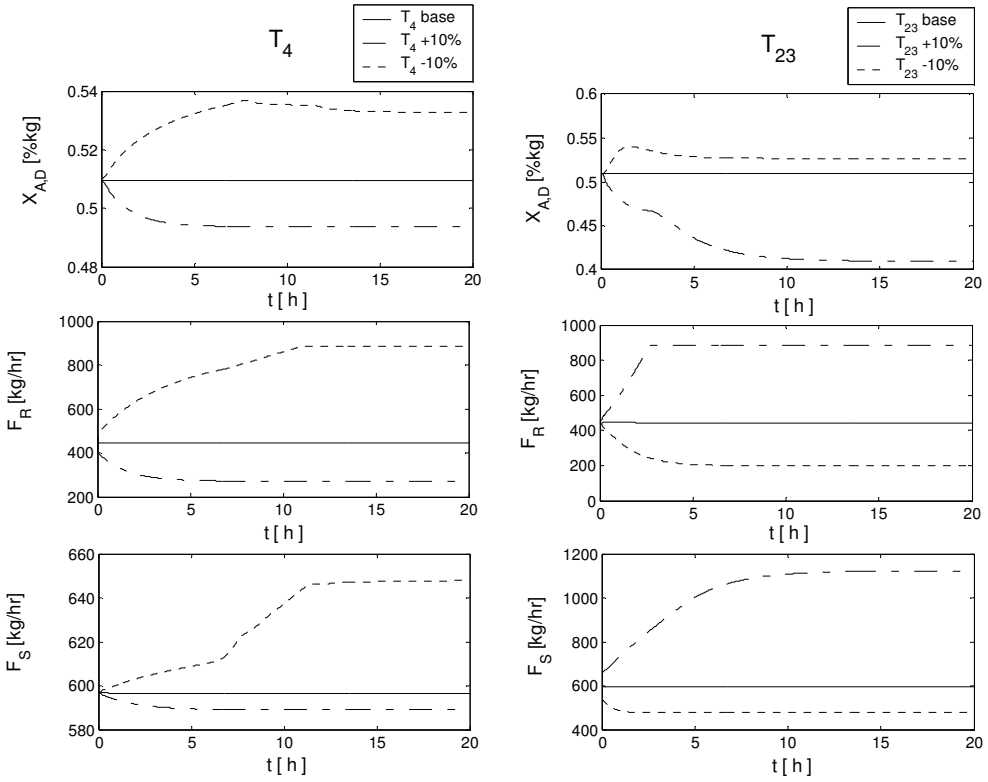


Figure 5-22. Effects of set point changes on acetone recovery as well as reflux and steam flowrates in the sidestream distillation design

5.5.2. Description of disturbance effects

This section aims to provide understanding the dynamic behaviour of distillation column in relation to the occurrence of disturbances in the investigated distillation unit. The magnitude of the disturbance effects should reflect whether the control scheme can handle disturbances properly and thereby achieve consistent product quality and reduce production of costly off-spec product, or visa versa. Even though particular small disturbance may not have significant effect on the product quality, it is still necessary to determine which measure of disturbance could have worse effect on the product quality.

The discussion should also evaluate the chosen control structure to guarantee that process deviation associated with disturbances will not result in unacceptable plant disruption or emissions. Finally, the description of disturbances shall give a basic insight to propose an evaluation framework of a new risk associated with the improvement design in distillation technology. For that reason, therefore, this section will be separated into three parts to discuss concerning some possible consequences on:

- production problem
- operating problem
- sidestream disturbance problems

The base case distillation design is used in the simulation for the purpose of illustration for production and operating problems, while sidestream design is used in the simulation for illustrating sidestream disturbance. The external flows (cooling water flowrate, reflux flowrate and steam flowrate) are considered to be the source of the disturbances in the simulation of case study. This is due to the fact that, from control point of view, that distillation columns are usually higher interconnection, and thus a change in any point (e.g. reflux or heat input) generally affects the output.

The disturbances are categorized into higher, lower and medium level disturbances and the dynamic responses are evaluated. All disturbance analysis are investigated by changing of - 50%, -10 % and 50% from the original value, as the lower, medium and higher levels of disturbance. The application of different level of disturbances in this dynamic simulation can provide necessary information about correlation between the level of disturbances and the degrees of severity in the distillation process operation. The running time for the simulation is 20 hours. For this section, the base case column is used for the application of disturbance simulation for the purposes of illustration.

Some remarks should be noted here that:

- This simulation did not include inert gas in feed stream.
- Information concerning the capacity of reflux pump is required in order to guarantee that reflux flowrate is supplied sufficiently when the reflux controller responses to higher temperature of column tray after cooling water reduction.
- Column capacity limits are not checked. This dynamic simulation does not consider effects of weeping, flooding and pressure drop.

5.5.2.1. Disturbance examples

5.5.2.1.1 Blockage of vent line and pressure controller/cooling water failure

Figure 5-23 shows the illustration of the disturbance on cooling water flowrate. The reduction of cooling water flowrate may be caused by blockage of vent line and failure of pressure control loop. Effects of disturbance on control behaviour, process and safety are investigated. The discussion will present the effects of disturbance due to reduction or increase of cooling water flow rate. The amounts of cooling water disturbance investigated are 10%, 20%, 30% and 50% reduction and 50% increasing in flowrate.

10% reduction of cooling water flowrate

Control behaviour
The controller action is set as "direct acting" in ASPEN dynamic control configuration for level, pressure and rectification section temperature controllers, while the controller action is set as "reverse acting " for bottom section temperature controller. Bottom level is controlled by base stream and condenser level is controlled by distillate flowrate.

- Figure 5-25A shows that as cooling water flowrate decreases to 10%, pressure increases. At the beginning, pressure is at set point pressure of 1.01 bar. After cooling water reduces to 10%, the pressure increases into 1.07 bar. This is obvious since top column pressure is determined by the accumulation of material in vapour phase. Since column pressure is defined by directly changing the amount of material in vapour phase of overhead or by changing the rate of condensation of the overhead, therefore, reducing the rate of condensation leads to increasing column pressure.

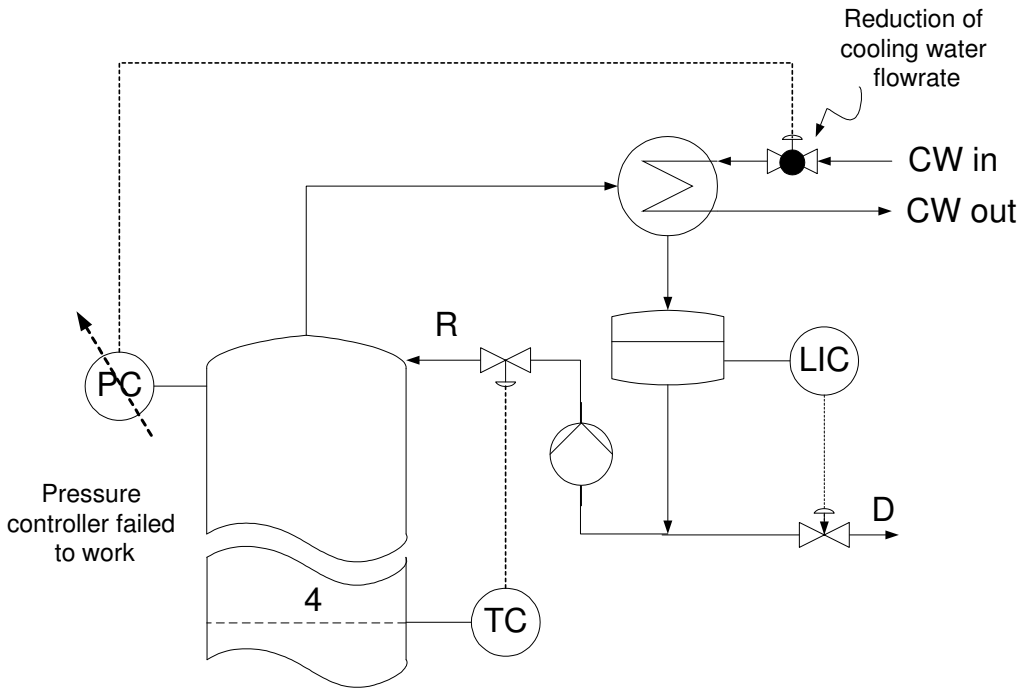


Figure 5-23. Illustration of the upper part of the distillation unit

- Figures 5-25D and 5-25E show that all level controllers work properly, where all controllers maintain their setpoints after the disturbance occurred.
- Figure 5-25H shows profile of reflux flowrate vs temperature on tray 4.
- As steam flow rate reduces (figure 5-25G), reflux flowrate reduces as well (figure 5-25H). It means, less steam requires less reflux. Therefore, an improvement of control concept can safe energy requirement if constraints are fulfilled.
- Figure 5-25B shows that the reduction of cooling medium will lead to increasing distillate temperature. This situation will propagate an accumulation of vapour in the condenser. This refers to following condenser duty equation:

$$\dot{Q}_{cond} = \dot{m} \cdot c_p \cdot \Delta\theta_c = k \cdot A \cdot \Delta\theta_m \qquad (5\text{-}11)$$

According to equation 5-11, with a constant heat capacity (c_p) of water and overall heat transfer (k) coefficient of condenser, as cooling water decreases, temperature gradient for cooling water increases. Due to increasing temperature gradient of cooling water, distillate temperature increases as well. The illustration in figure 5-24 below shows the temperature driving force profile via condenser length for stationary condition before and after disturbance.

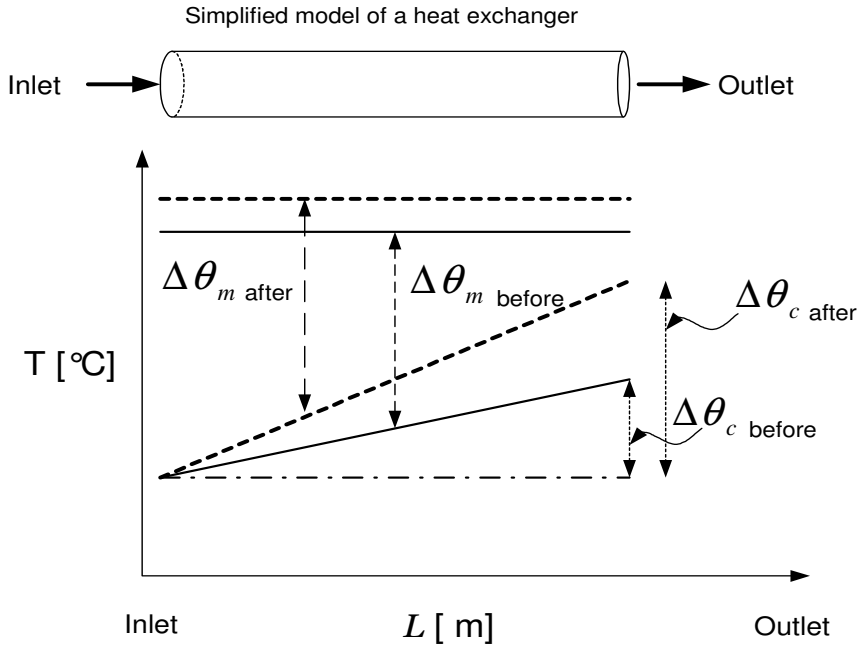


Figure 5-24. Illustration of a relationship between temperature driving force and the length of condenser-cooling medium contact. L, $\Delta\theta_c$ and $\Delta\theta_m$ represent distance along the condenser, temperature gradient for cooling water and temperature driving force, respectively

- Figure 5-25G shows that 10% cooling water reduction propagate temperature controller to react. As cooling water decreases, temperature on tray 20 increases and accordingly steam flowrate decreases.

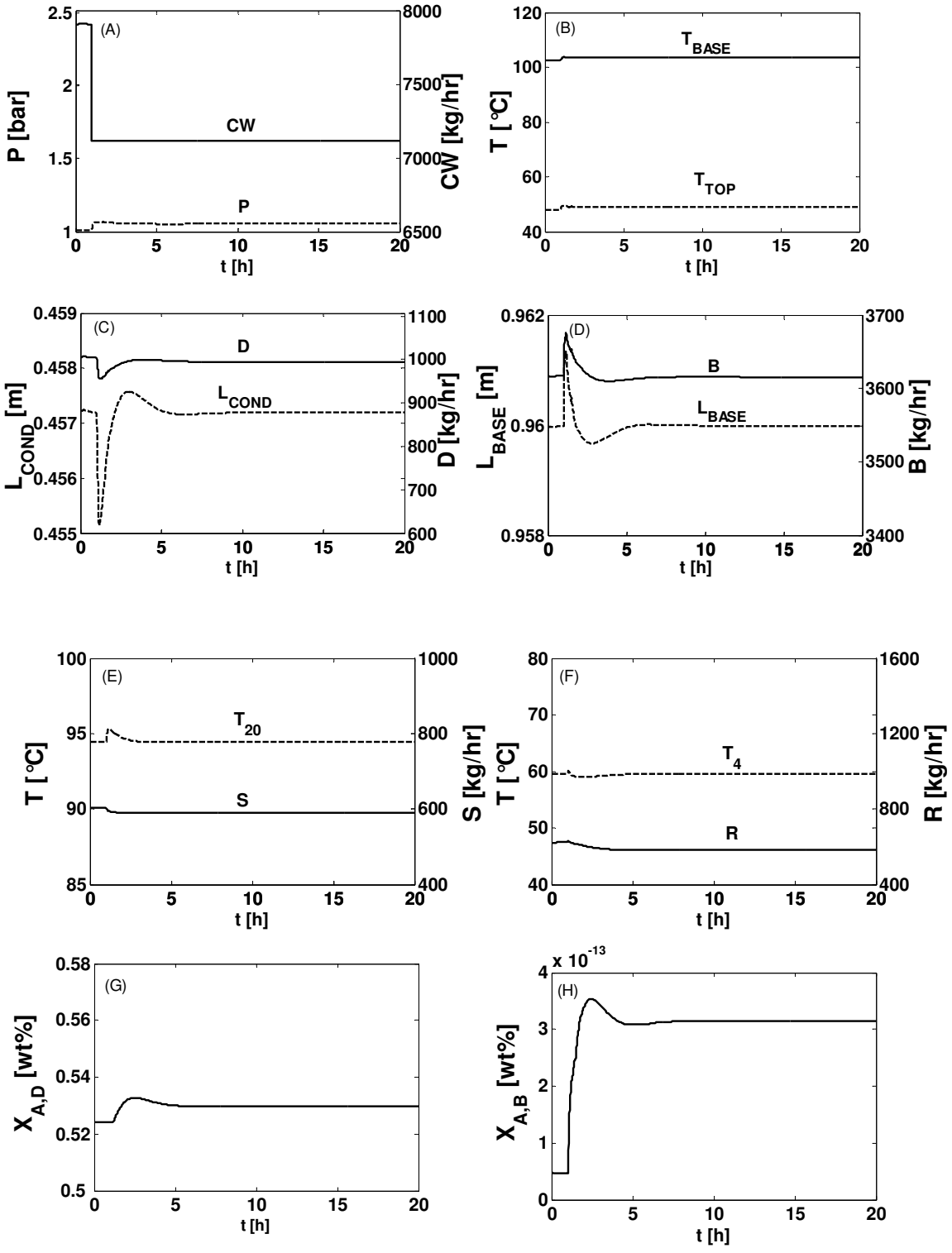


Figure 5-25. Investigation of effects due to 10% reduction of cooling water flowrate. Temperature sensor locations at trays 4 and 20

Consequences to products

- The effects of disturbance on plant process are indicated by the behaviour of temperature and composition profiles as shown in figure 5-25B, C, F and I.
- Figure 5-25B shows that as 10% of cooling water flowrate reduces, temperature on bottom and top columns increase by 2°C.
- Figures 5-25C, 5-25F and 5-25I show the profile of product qualities. Figure 5-25C shows that, acetone purity in distillate increases from 53 wt% to 54 wt% which is within the purity target ($X_{A,D} > 50\%$). Figure 5-25F shows that, water impurity in distillate reduces from 2.9 wt% to 2 wt%, which is within the product impurity target ($X_{W,D} < 10\%$). Figure 5-25I shows that, acetone impurity in base stream increases small from 10^{-5} wt% to 10^{-4} wt%. The maximum limit of acetone in base stream is 2% and therefore acetone mass fraction is still far from the limit.

Consequences to safety/ environment

- The observed pressure profile is the indication for the safety level of the column. The pressure profile is compared with the design pressure. Figure 5-25A shows the profile of column pressure. The maximum pressure observed is lower than design pressure (3 bars). Therefore, safety is maintained under this disturbance.
- Like the pressure profile, the temperature profile from dynamic simulation must also be investigated and compared with design temperature. Figure 5-25B shows that there is no relevant change in temperature (2°C) and operation temperature is much lower than design temperature (150 °C).

20% reduction of cooling water flowrate

Summary of control behaviour and consequences generated

Figure 5-26 shows results of investigation for disturbance due to 20% reduction of cooling water. This figure tells that, the direction of response of pressure, level and temperature controllers for this disturbance have similar response as 10% reduction of cooling water flowrate. While the behaviour of the response is similar, the different is only a matter of magnitude of the effects. Therefore, detail explanation follows the discussion of 10% reduction of cooling water.

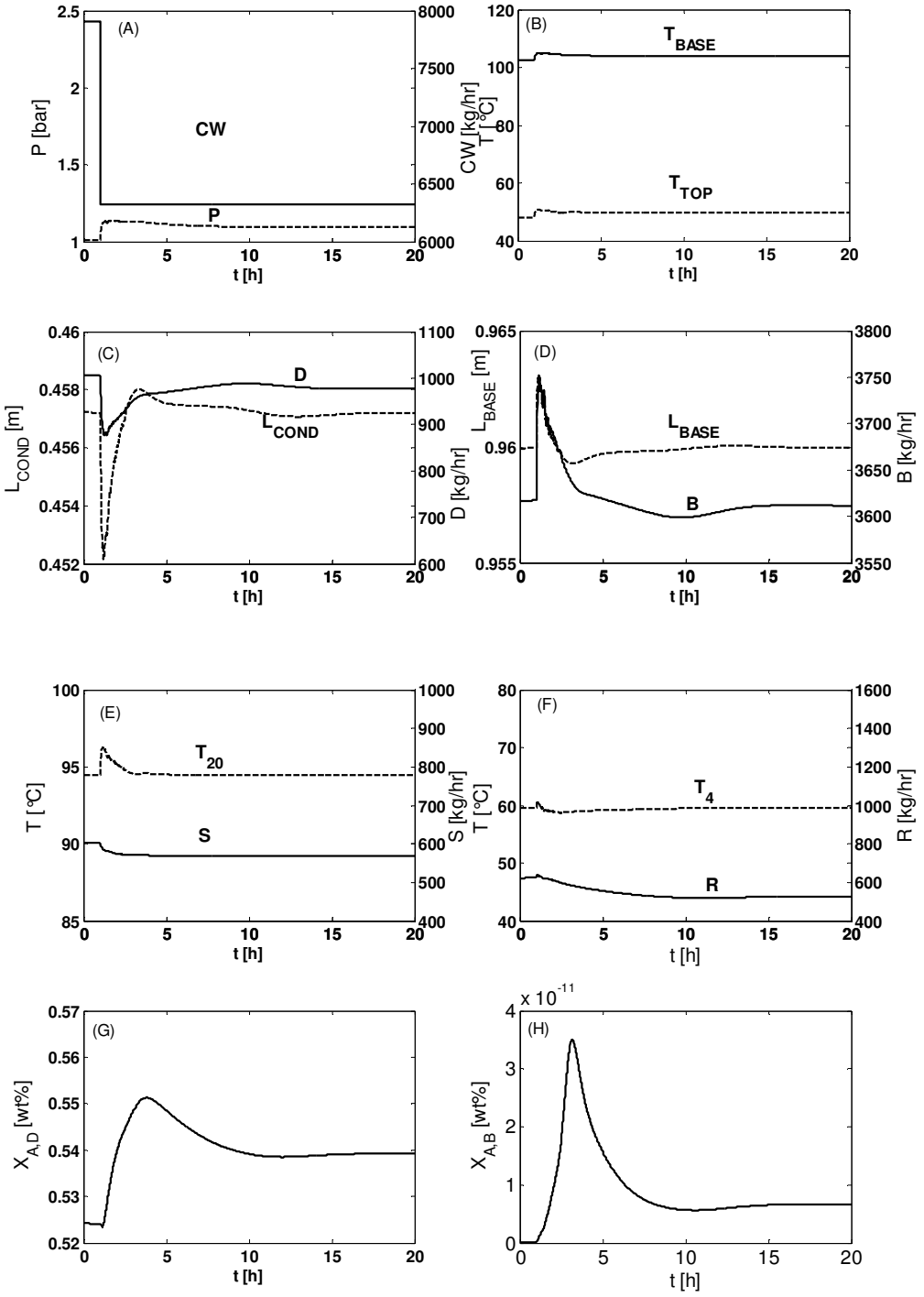


Figure 5-26. Investigation of effects due to 20% reduction of cooling water flowrate. Temperature sensor locations are tray 4 and 20

30% reduction of cooling water flowrate

Control behaviour

- Figure 5-27A shows that as 30% of cooling water flowrate decreases, pressure increases. At the beginning, pressure is at set point pressure of 1.01 bars and it increases to 2.2 bars after 30% of cooling water reduced. As pressure increases, temperature of bottom and top column increases as well (figure 5-27B). Column pressure is defined by condenser condition.
- At 2.2 bars this pressure, temperature driving force is big enough to reach a new stable point.
- Figures D and E show that all level controllers work properly, where all controllers maintain their setpoints after the disturbance occurred (figure 5-27D and 5-27E).
- Figure 5-27H shows that as temperature at tray 4 increases, reflux flowrate increases. The profile of reflux flowrate in figure 5-27H tells that reflux flowrate reached predefined maximum to response an increasing temperature on tray 4.
- The profile of reflux flowrate (figure 5-27H) shows an instability in control concept when reflux flowrate responses to compensate increasing temperature. It is shown that the disturbance rejection is limited by limitation of the capacity of reflux flowrate. Since the reaction of controller depends on the temperature profile, it seems that set point temperature at tray 4 is too low.
- Another explanation of malfunction of control concept is based on figure 5-27G. Because of the disturbance, lower volatile components reach the controlled tray, temperature goes down. At this condition, much higher steam is necessary to stabilize control.
- As explained earlier, higher pressure shifts temperature profile as shown in figure 5-27B, 5-27G and 5-27H. The direction of temperature profile (which goes down) when pressure increased is uncommon condition. This is because the higher driving force associated with this pressure change. This higher pressure change results instability. Figure 5-27G and 5-27H show that temperature profiles are more sluggish implying that temperature set points on these controllers are not optimum. Alternatively, the controller location should have been changed into a location closer to base to reduce effect of disturbance on the controlled tray.

Consequences to products

- Figure 5-27B shows that as cooling water flowrate reduces to 30%, temperature on bottom and top columns increase. The column reached maximum temperature of 124°C which is still below the design temperature (150°C).
- Figures 5-27C, 5-27F and 5-27I show the profile of product qualities after 30% reduction of steam flowrate. Figure 5-27C shows that, as 30% of cooling water flowrate reduces, acetone purity in distillate increases from 53 wt% to 56 wt% which is within the purity target ($X_{A,D} > 50\%$). Figure 5-27F shows that, as 30% of cooling water flowrate reduces, water impurity in distillate increases after 20 hours from 2.9 wt% to 3.5 wt%, which is within the product impurity target ($X_{W,D} < 10\%$). Figure 5-27I shows that, as 30% of steam flowrate reduces, acetone impurity in base stream increases. Therefore, the distillate and bottom product qualities are still achieved even the disturbance of 30% cooling water reduction occurred.

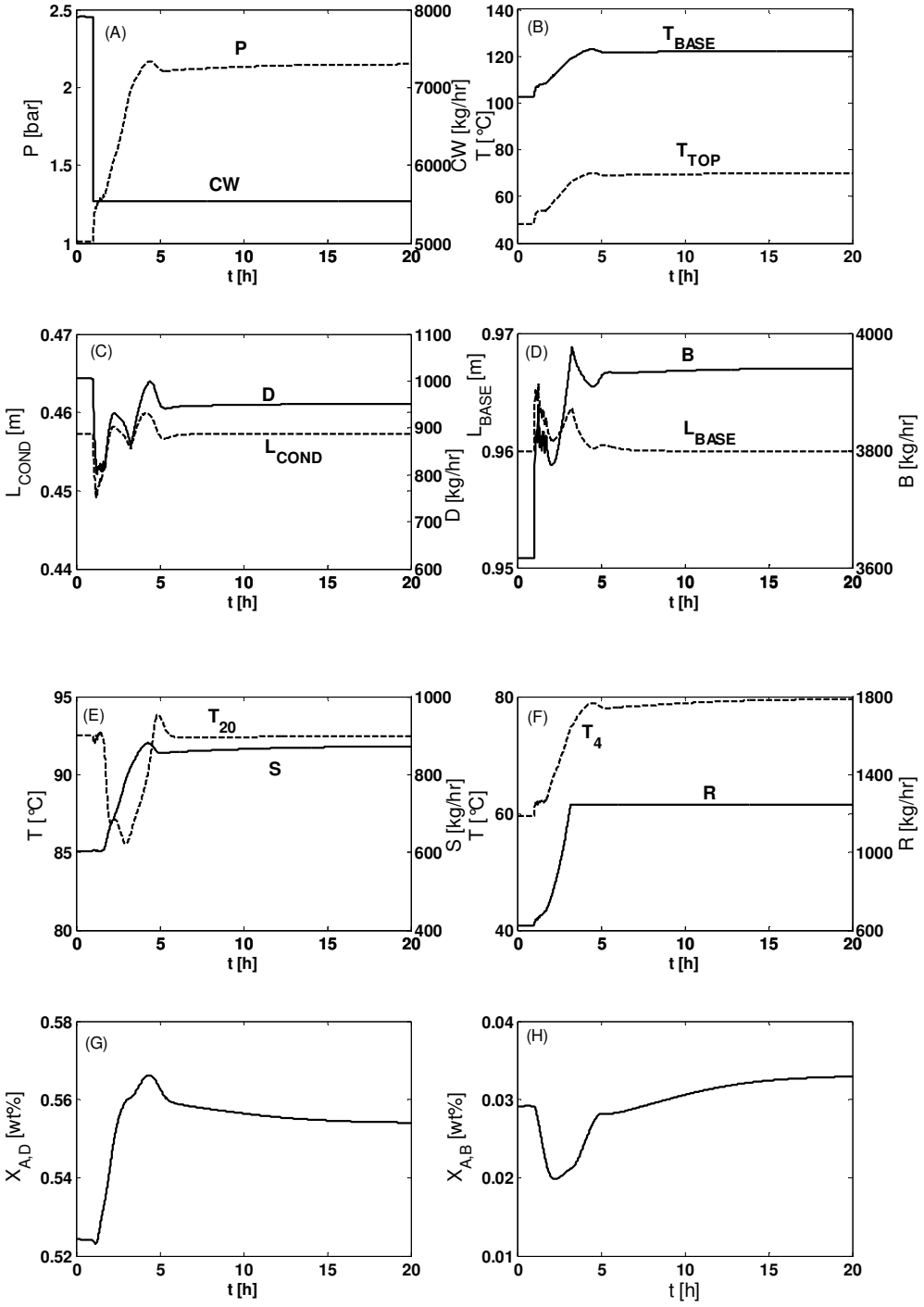


Figure 5-27. Investigation of effects due to 30% reduction of cooling water flowrate. Temperature sensor locations are at tray 4 and 20

- Figure 5-27A shows the profile of column pressure after reduction of 30% cooling water flowrate. The column reached maximum pressure of 2.2 bars. From that pressure, it is obvious that that pressure is still operating below the design pressure (3 bars) even disturbance of 30% of cooling water flowrate occurred. Therefore, it is estimated that column safety is guaranteed under this disturbance.
- Figure 5-27B shows temperature profile of top and base column after cooling water disturbance. This figure shows that 30% reduction of cooling water will lead to increasing temperature but not violate design temperature limit (150°C).

Finding optimum controller locations / temperatures set points

Following the findings from previous studies of disturbances, an improvement is made to find optimum tray.

Figure 5-28A demonstrates dynamic behaviour of the original control system as discussed before (see figure 5-27). Figure 5-28C demonstrates dynamic behaviour of modified control system that means the controlled trays are 8 instead 4 for rectification section and 31 instead of 20 for bottom section.

As cooling water reduces at time = 1 hour, temperature at tray 8 reduces and turn again into original. Also, steam flowrate reduces to compensate increasing temperature at tray 31.

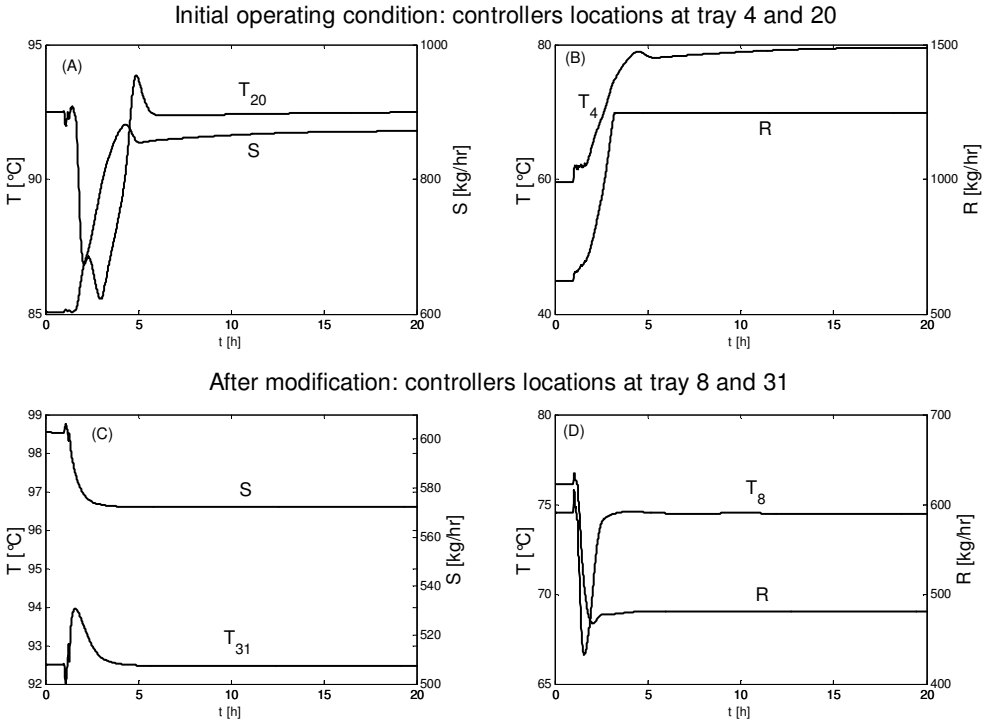


Figure 5-28. Comparison of different temperature sensor location to response on 30% of cooling water reduction

Figure 5-29 shows dynamic behaviour of the column after 30% reduction of cooling water flowrate. The dynamic profiles in figure 5-29 tells that, the direction of response of pressure, level and temperature controllers for this disturbance have similar response as 10%

and 20% reduction of cooling water flowrate. While the behaviour of the response is similar, the different is only a matter of magnitude of the effects. It means, column still can withstand with 30% reduction of cooling water and controllers work properly to maintain the expected behaviour of the column. For the detail explanation, therefore, this section follows the discussion of 10% reduction of cooling water.

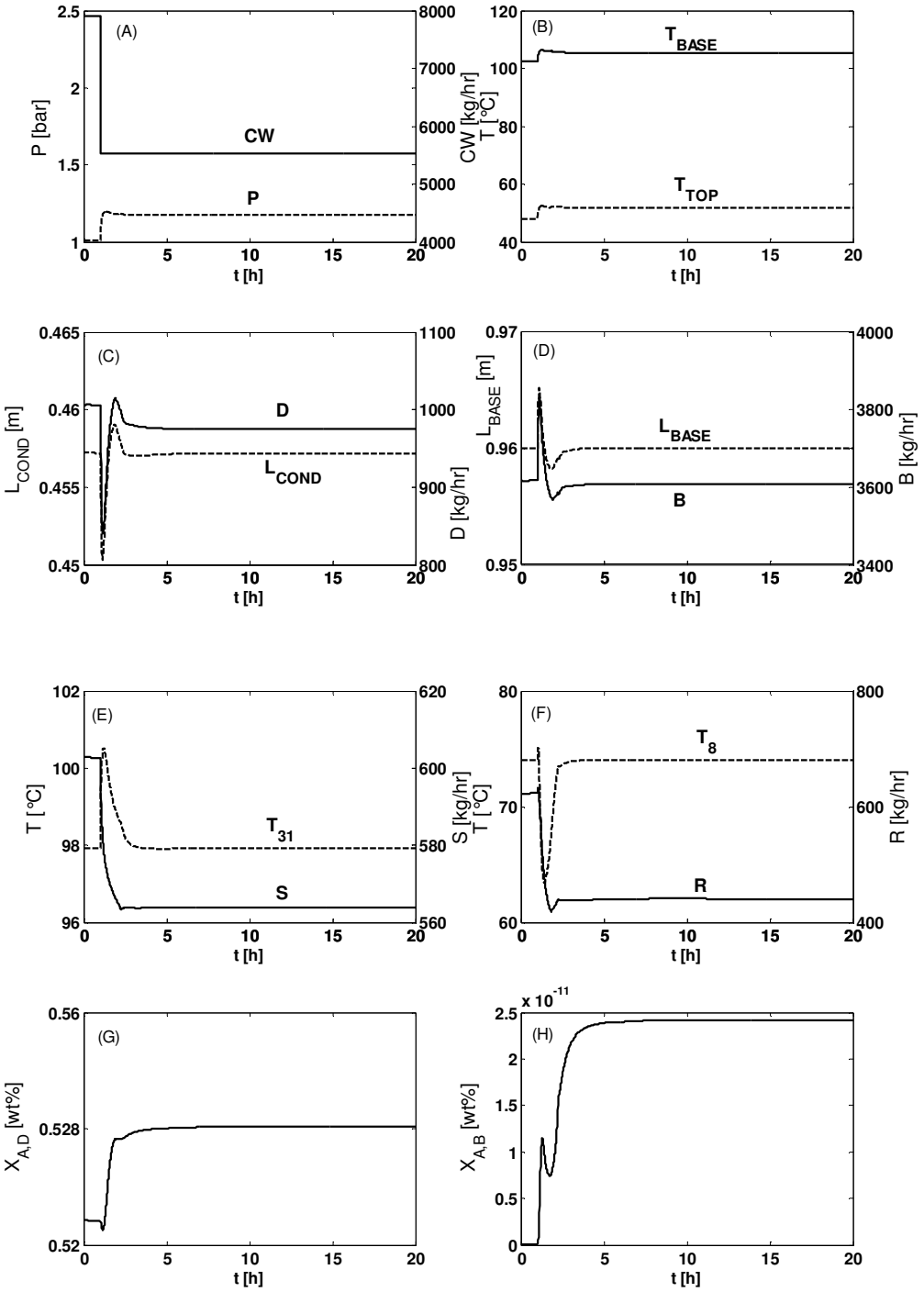


Figure 5-29. Optimum dynamic behaviour after 30% reduction of cooling water flowrate. Temperature sensor locations are at trays 8 and 31

50% reduction of cooling water flowrate

Summary of control behaviour and consequences generated

The dynamic profiles in figure 5-29 tells that, the direction of response of pressure, level and temperature controllers for this disturbance have similar response as 30% reduction of cooling water flowrate with nonoptimum controller concept. It shows the instability phenomena in controller concept that has been explained already in the case of 30% reduction of cooling water flowrate. Therefore, the explanation of such dynamic behaviour follows the explanation for 30% reduction of cooling water with nonoptimum tray location.

Figure 5-30A shows that as 50% of cooling water flowrate decreases, pressure increases from of 1.01 bars into 2.9 bars. At this pressure, temperature driving force is big enough to reach a new stable point (figure 5-30H). The maximum pressure is 2.9 bars, which is close to the design pressure.

Figure 5-30A shows that as 50% of cooling water flowrate decreases, pressure increases from of 1.01 bars into 2.9 bars. At this pressure, temperature driving force is big enough to reach a new stable point (figure 5-30H). The maximum pressure is 2.9 bars, which is close to the design pressure.

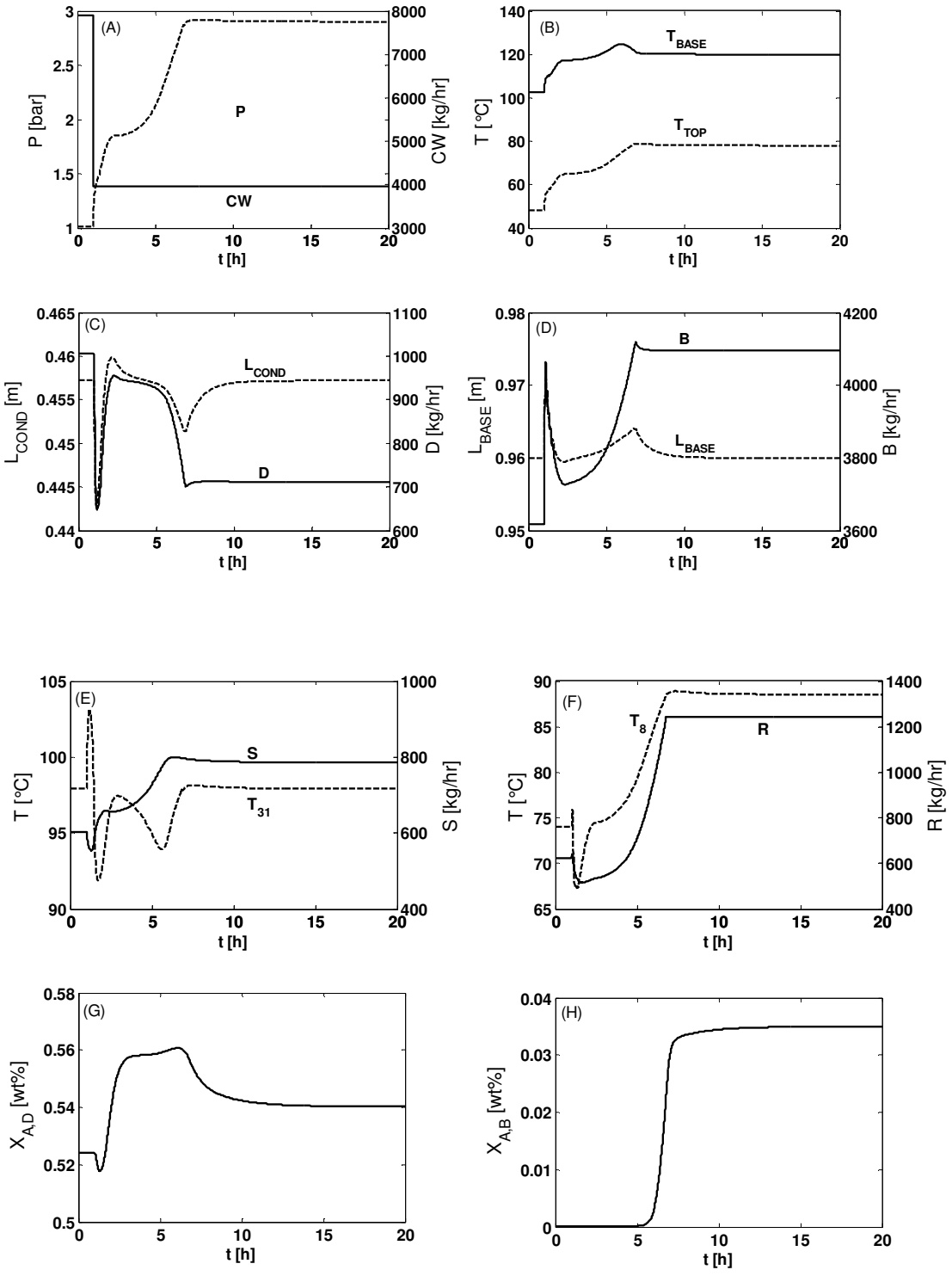


Figure 5-30. Investigation of effects due to 50% reduction of cooling water flowrate. Temperature sensor locations are at tray 8 and 31

50% increasing of cooling water flowrate

Control behaviour

- Figure 5-31 shows the investigation of effects due to 50% increase of cooling water flowrate**.** Figure 5-31A shows that as 50% of cooling water increases, pressure reduces from 1.01 bar to 0.9 bar. This reduced pressure results in decreasing temperature at the column, as shown in figure 5-31B.
- As shown in figure 5-31B, as cooling water increases, top and bottom temperatures reduce. Reducing pressure leads to increasing temperature at tray 8, as shown in figure 5-31H. The temperature in tray 31 reduces, thus steam flowrate increases to compensate for lowering temperature at tray 31, as shown in figure 5-31G. Figure 5-31F shows that steam increase results in high water in distillate as controled tray at tray 8 increases. Consequently, temperature at tray 8 increases. This results in increase of reflux flowrate as well.
- Figure 5-31D and E show that as bottom and condenser levels decrease/ increase, distillate and bottom flowrates react to maintain the levels.
- Figure 5-31 tells regarding the complexity of dual temperature control. The main source of affecting control loop comes from steam flowrate/ base column control. Therefore, distillate product quality is affected significantly due to change of steam flowrate. It should be taken into account that if product quality is higher than usual, then it requires more steam and accordingly, it expenses more operating cost. Therefore, reduction of top column pressure requires a reduction of temperature set points to achieve the same product quality as before.

Consequences to products

- Figure 5-31C shows that as 50% of cooling water increases, acetone mass fraction in distillate decreases. Such acetone purity in distillate is most affected by higher temperature setpoint and higher steam flowrate. Therefore, an improvement on acetone mass fraction will be obtained through reducing setpoint temperature, thus results in better quality of acetone in distillate. Figure 5-31F shows that as 50% of cooling water flowrate increases, water impurity increases for short time.
- The profile of acetone mass fraction as shown in figure 5-31C tells that the bottom quality is achieved even it reduces after 50% increasing of cooling water flowrate. It is shown that the amount of acetone mass fraction is still within the target (>50 wt%). Since the cost of steam consumption is expensive, therefore, a trade-off between steam flowrate and the quality of acetone mass fraction in base stream should be considered to reduce steam flowrate even results in increasing the amount of acetone mass fraction in bottom stream. The decision of minimum steam flowrate should be made until acetone mass fraction is still lower than the target (<2 wt%). Change of acetone in bottom is from mass fraction of 10^{-4} to mass fraction of 10^{-5}.

Consequences to safety/ environment

Figure 5-31 shows that pressure reach the pressure below the set point. This condition results in a vacuum condition. Thus, some potential safety related problems arise if vacuum exists. Due to this pressure reduction, it is not possible to empty/flow the distillate product from catch tank through hydrostatic. This results in flooding the condenser and accordingly column and e.g. in air reflux flow. To solve this problem, one result could be opening the vent line and remove blockage.

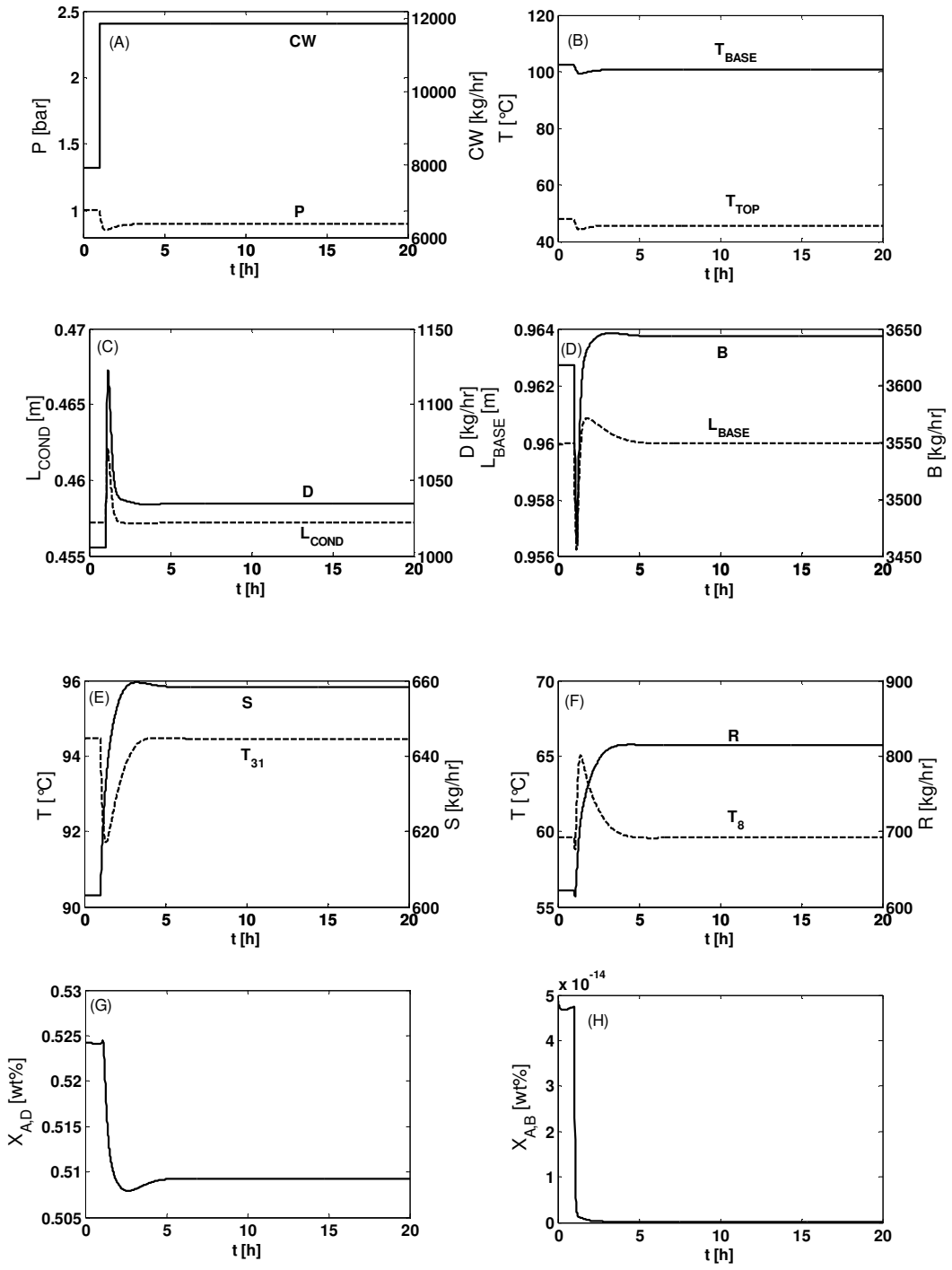


Figure 5-31. Investigation of effects due to 50% increase of cooling water flowrate. Temperature sensor locations are at tray 8 and 31

5.5.2.1.2 Steam disturbance and failure of temperature controller

Figure 5-32 shows the illustration of disturbance on steam flowrate. Effects of disturbances on control behaviour, process and safety are investigated. Steam is injected directly as the heat source of separation. The disturbance is performed through the addition of disturbance task in ASPEN dynamic. Temperature controller is changed from automatic control to manual controller. Steam flowrate is changed. Temperature controllers are at tray 8 and 31 for rectification section and bottom section temperature controllers.

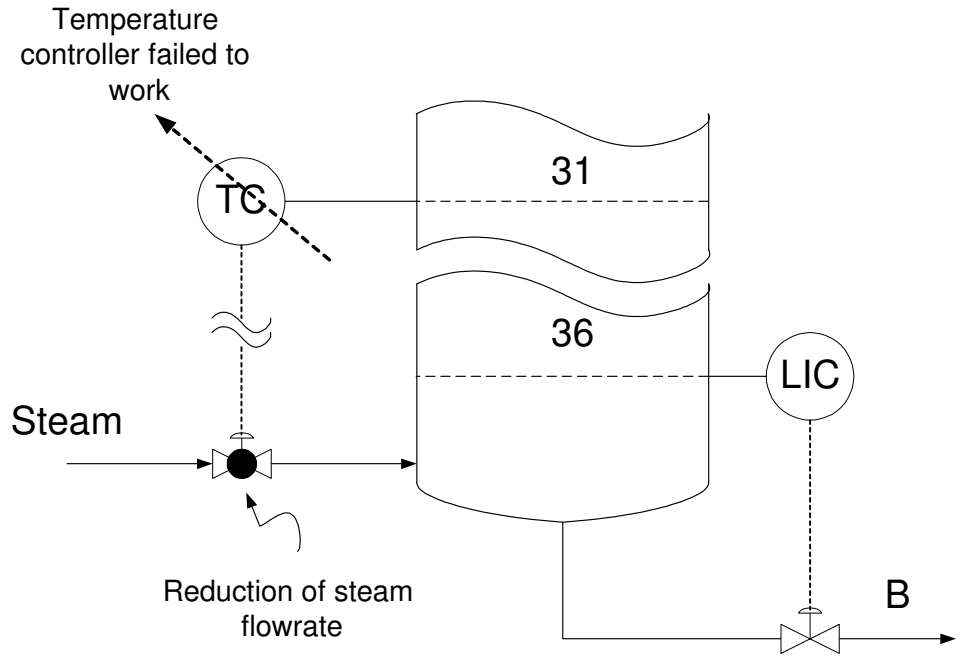


Figure 5-32. Illustration of the bottom part of the distillation unit.

10% reduction of steam flowrate

Control behaviour
▪ At normal condition, steam flowrate is 603 kg/h at base. After 1 hour operation time, 10% of steam flowrate is reduced. Figure 5-33D and 5-33E show that all level controllers work properly. All controllers maintain their setpoints level after the disturbance occurred. In this case, as shown in figure 5-33D and 5-33E, distillate and bottom flowrates decrease. This is obvious since the steam is injected directly to the column and thus, column will maintain material balance within the whole column as steam flowrate reduces.
▪ Figure 5-33A shows that as 10 % of steam flowrate decreases, pressure remains around the set point. It means, pressure controller works properly. Top column pressure is controlled by manipulating cooling water flowrate.
▪ An interesting dynamic behaviour is shown from the profile of cooling water requirement as shown in figure 5-33A. As steam flowrate reduces, cooling water flowrate reduces.
▪ Figure 5-33B shows that, temperature in top and base column reduces. Temperature at top decreased from 48°C to 47°C, while temperature at base decreased from 102°C to 100°C.

- Figure 5-33G shows temperature at tray 31 decreases since temperature controller at tray 31 did not work to response on temperature change. Figure 5-33H shows temperature at tray 8 decreases. As a response, reflux flowrate decreases as well.
- Reducing steam flowrate causes reducing water fraction in distillate. Because of this, temperature at tray 8 reduces and thus propagate temperature controller at tray 8 to reduce reflux flowrate. Since temperature at tray 31 reduces, acetone mass fraction in the base increases.

Consequences to products

- The effects of disturbance on plant process are indicated by the behaviour of temperature and composition profiles as shown in figure 5-33B, C, F and I.
- Figure 5-33B shows that as 10% of steam flowrate reduces, temperature on bottom and top columns reduce by 1°C.
- Figures 5-33C, 5-33F and 5-33I show the profile of product qualities. Figure 5-33C shows that, acetone purity in distillate increases from 53 wt% to 54 wt% which is within the purity target ($X_{A,D} > 50\%$). Figure 5-33F shows that, water impurity in distillate increases from 2.9 wt% to 3.8 wt%, which is within the product impurity target ($X_{W,D} < 10\%$). Figure 5-33I shows that, acetone impurity in base stream increases until 0.5 wt%. The maximum limit of acetone in base stream is 2% and therefore acetone mass fraction is still far from the limit. Since reducing heat supply into the column leads to increasing the high volatile component in the base, therefore the increasing of acetone mass fraction in the base is an obvious effect of reducing steam flowrate.

Consequences to safety/ environment

- Figure 5-33 shows that pressure still operates within the setpoint of 1.01 bar after 10% reduction of steam flowrate. This pressure is still far from design pressure of 3 bars. The safety related problem does not exist due to 10% reduction of steam flowrate. The same condition is also true for temperature changes in the column. It is shown from temperature profiles in figure 5-33B that pressure is still below design temperature of 150°C.
- Figure 5-33I shows that as 10% reduction of steam flowrate reduces, acetone mass fraction in the base increases. This increasing trend of high volatile component in the base stream is an indication that reducing steam flowrate will tend to generate problem on environmental impact. Thus, the consequence of potential environmental impact arises as steam flowrate reduces.

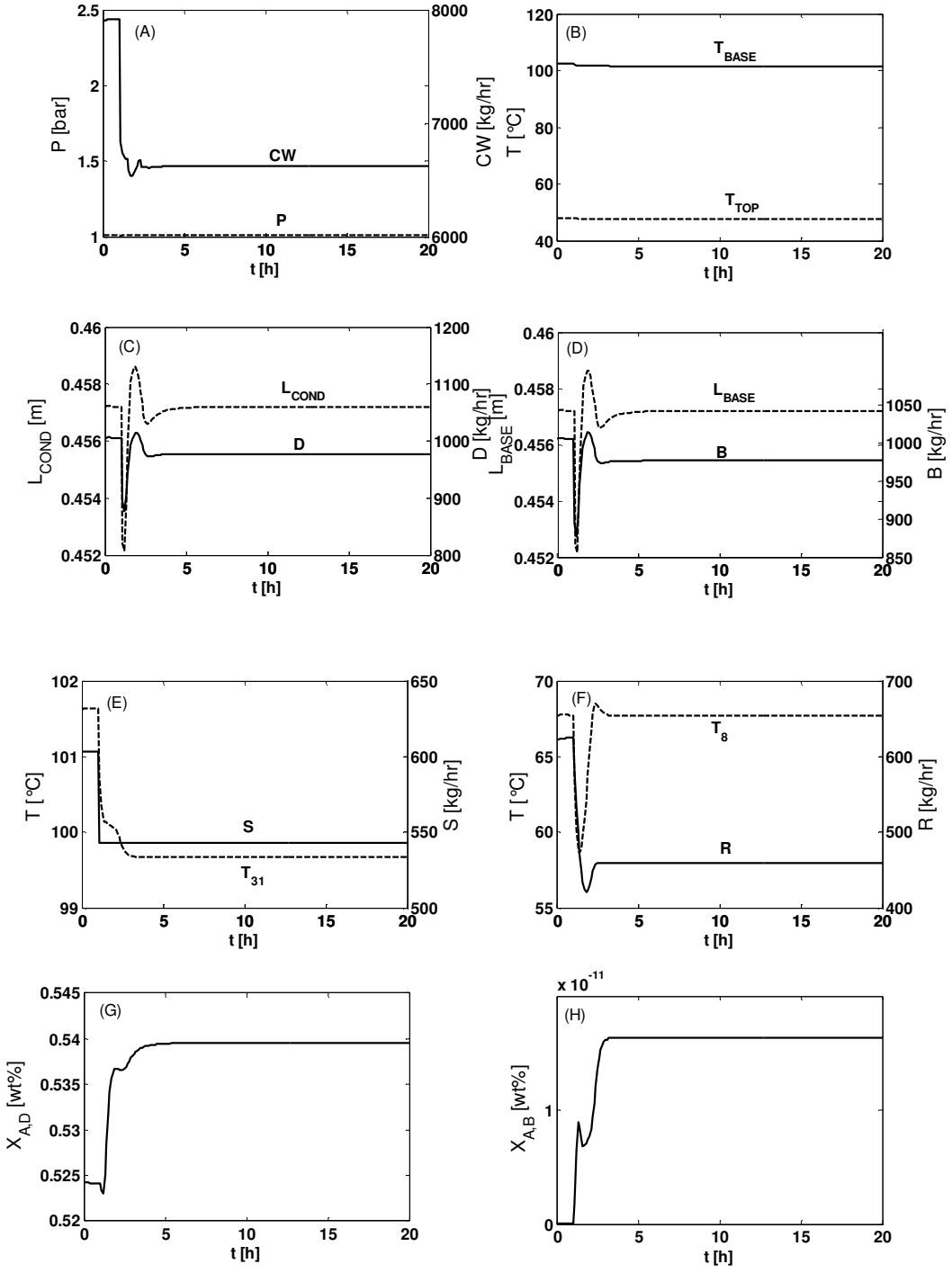


Figure 5-33. Investigation of effects due to 10 % reduction of steam flowrate.

20% and 30% reduction of steam flowrate

Summary of control behaviour and consequences generated

Figure 5-34 shows results of investigation for disturbance due to 20% reduction of steam flowrate. Whereas, Figure 5-35 show the results of investigation for disturbance due to 30% reduction of steam flowrate. These two figures tell that, the direction of response of pressure, level and temperature controllers for this disturbance have similar response as 10% reduction of steam flowrate. While the behaviour of the response is similar, the different is only a matter of magnitude of the effects. Therefore, detail explanation follows the discussion of 10% reduction of steam flowrate.

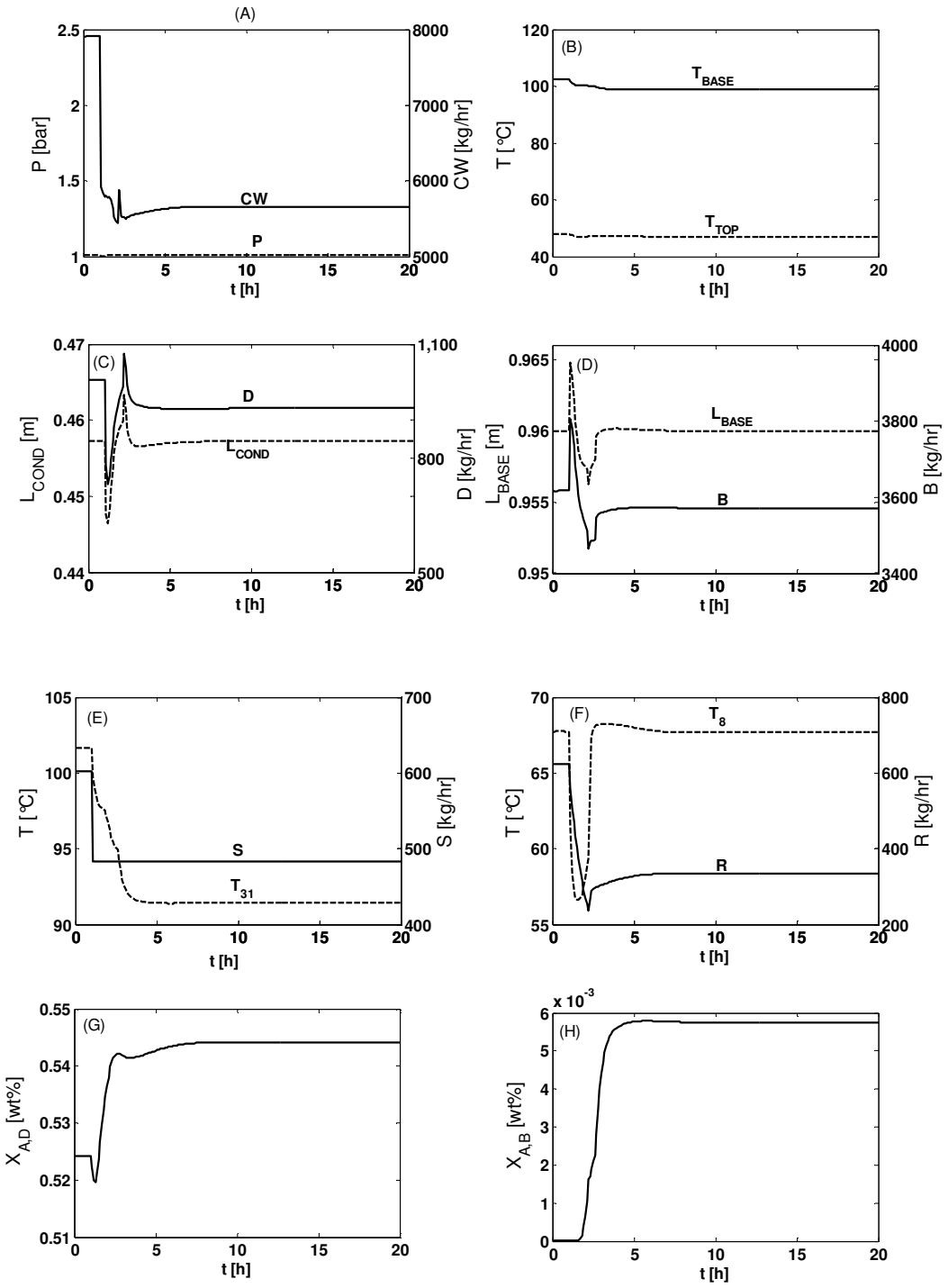


Figure 5-34. Investigation of effects due to 20 % steam reduction

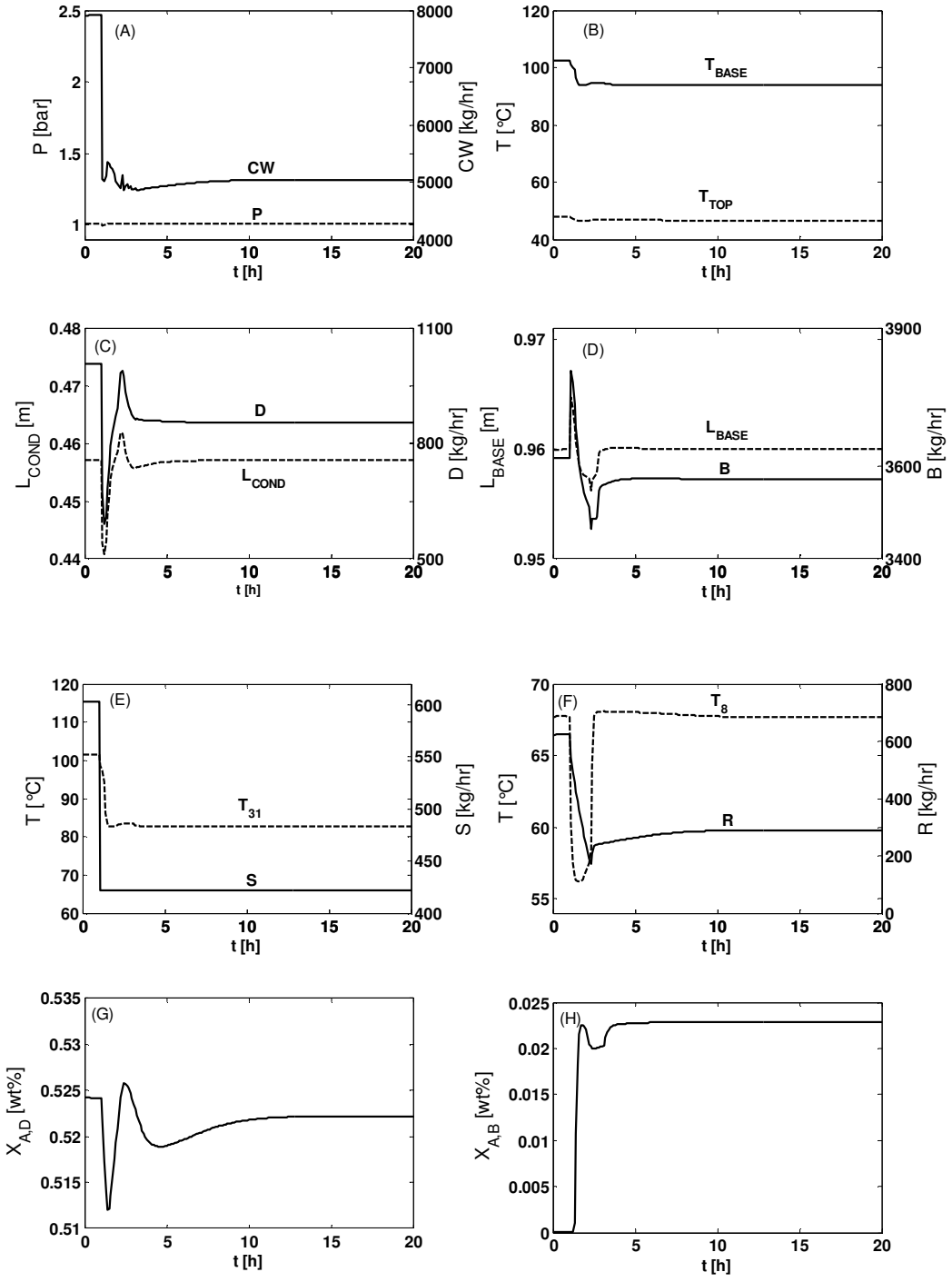


Figure 5-35. Investigation of effects due to 30 % steam reduction

50% reduction of steam flowrate

Summary of control behaviour and consequences generated

Figure 5-36 shows results of investigation for disturbance due to 50% reduction steam flowrate. This figure tells that, the direction of response of pressure, level and temperature controllers for this disturbance have similar response as 10%, 20% and 30% reductions of steam flowrate. However, the reduction of 50% of steam flowrate causes decreasing of top and bottom column by 10 °C and 5 °C respectively, as shown in figure 5-36B. This significant change might cause significant effects to tray temperatures and product qualities.

Figure 5-36C, 5-36I and 5-36F show the profile of product qualities. Figure 5-36C shows decreasing acetone mass fraction in distillate below the expected target (50 wt%). Whereas, 5-36F shows increasing acetone mass fraction in base stream above the expected target. Therefore, the most important effect due to 50% reduction of steam flowrate is the poor product qualities. It is reasonable since the lower stem flowrate, the lower high volatile component vaporises.

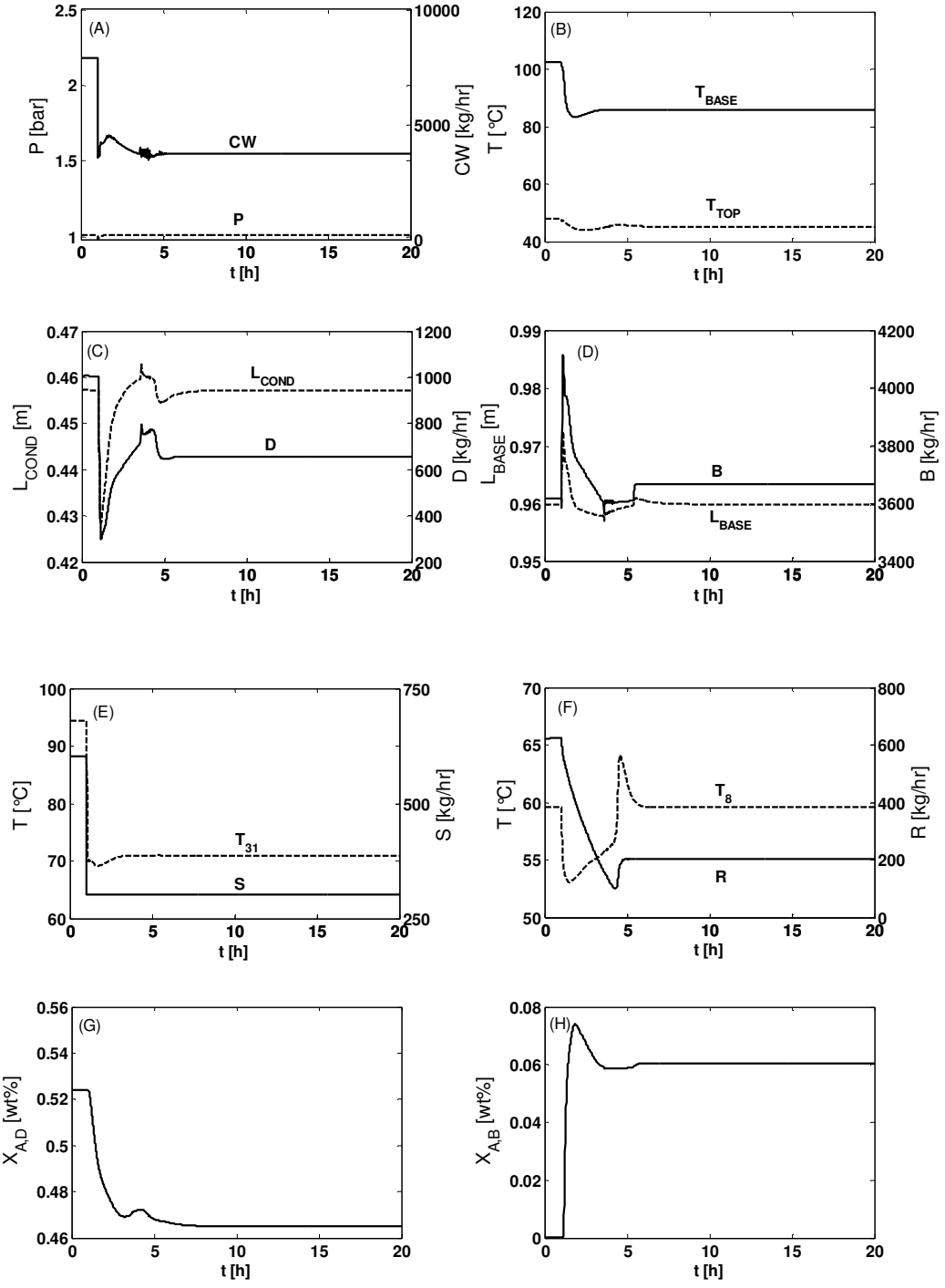


Figure 5-36. Investigation of effects due to 50% reduction of steam flowrate

5.5.2.1.3 Reflux disturbance and failure of temperature controller

Figure 5-37 shows the illustration of disturbance on reflux flowrate. Effects of disturbances on control behaviour, process and safety are investigated. Temperature controller is used to control temperature on tray 8 by manipulating reflux flowrate. The disturbance is performed through the addition of disturbance task in ASPEN dynamic simulation. The tray location for bottom control tray is at tray 31. Reflux flowrate is changed during the disturbance simulation.

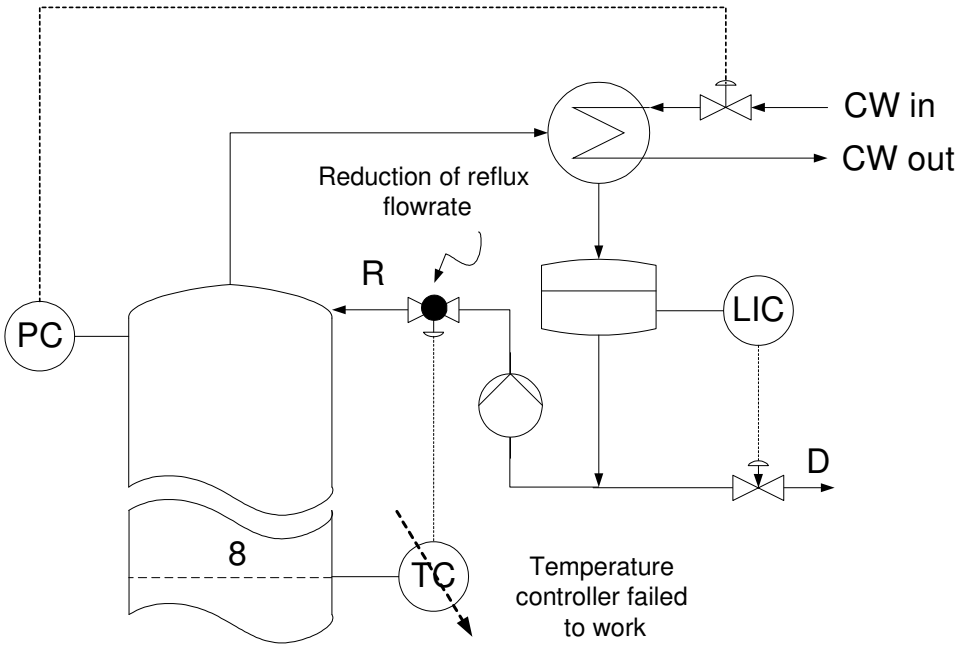


Figure 5-37. Illustration of the disturbance of reflux flowrate

10% reduction of reflux flowrate

Control behaviour
▪ At normal condition, reflux flowrate is 622 kg/h. After 1 hour operation time, 10% of reflux flowrate is reduced. Figure 5-38D and 5-38E show that all level controllers work properly. All controllers maintain their setpoints level after the disturbance occurred. In this case, distillate flowrate decreases (figure 5-38E). Column maintained material balance within the whole column as reflux flowrate reduces.
▪ Figure 5-38A shows that as 10 % of reflux flowrate decreases, pressure remains around the set point. It means that pressure controller works properly. Top column pressure is controlled by manipulating cooling water flowrate.

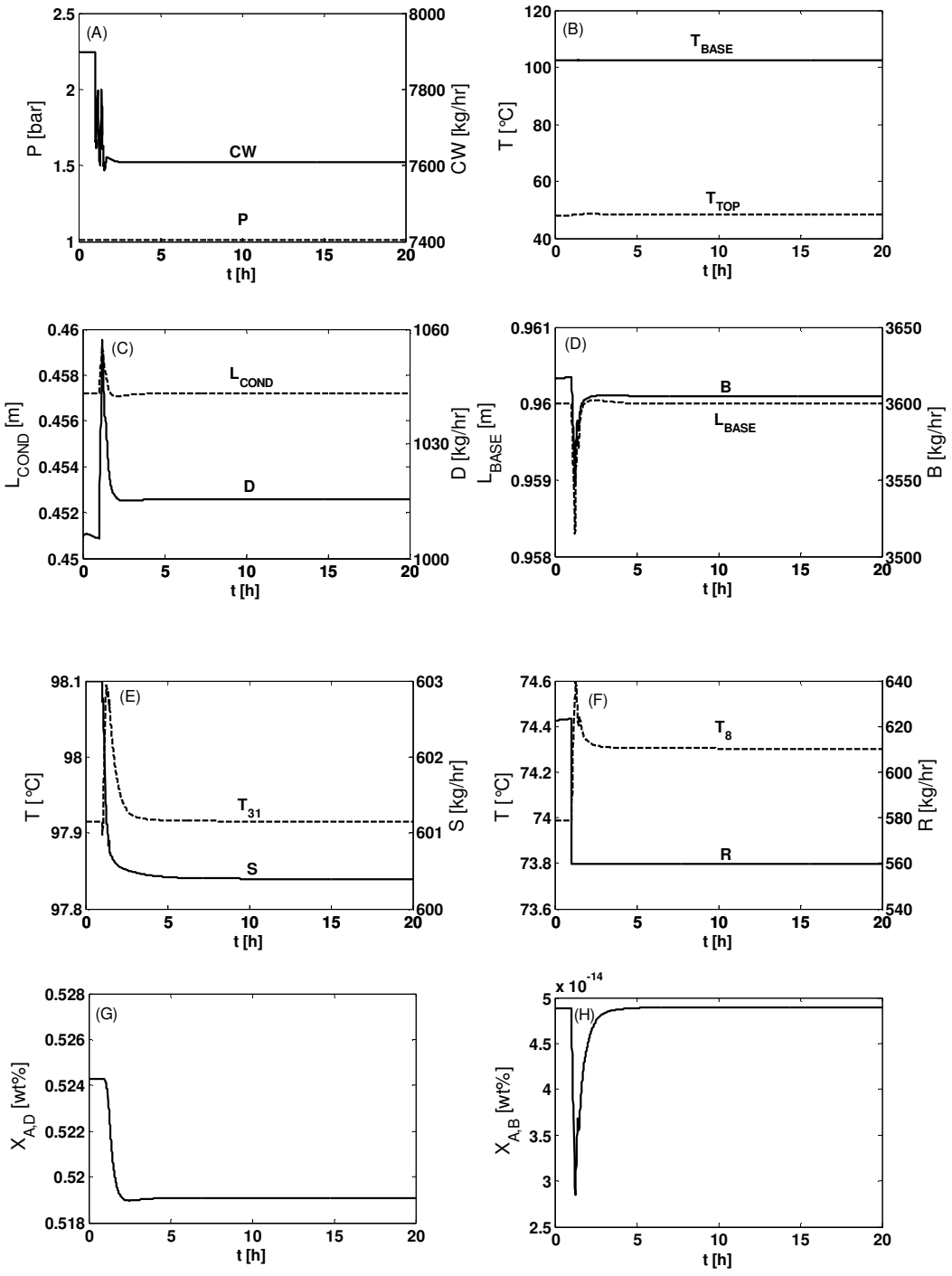


Figure 5-38. Investigation of effects due to 10% reduction of reflux flowrate

- The profile of cooling water requirement is shown from the profile of cooling water requirement as shown in figure 5-38A. As reflux flowrate reduces, cooling water flowrate reduces.
- Figure 5-38B shows temperature of top column increased slightly after 10% of reflux flowrate reduced.
- Figure 5-38G shows temperature at tray 31 increases slightly and propagate steam flowrate to decrease slightly as well. Figure 5-38H shows temperature at tray 8 increases as 10 % of reflux flowrate decreases. Due to reducing reflux flowrate, acetone mass fraction in distillate reduces.

Consequences to products

- The profile of temperature and composition profiles as shown in figure 5-38B, C, F and I.
- Figure 5-38B shows that as 10% of reflux flowrate reduces, temperature of bottom column increases whereas temperature of top columns remains constant. The increased temperature on top column is still far from the design temperature (150°C).
- Figures 5-38C, 5-38F and 5-38I show the profile of product qualities. Figure 5-38C shows that, acetone purity in distillate reduces from 53 wt% to 52 wt% which is still within the purity target ($X_{A,D} > 50\%$). Figure 5-38F shows that, water impurity in distillate increases from 2.9 wt% to 3.9 wt%, which is still within the product impurity target ($X_{W,D} < 10\%$). Figure 5-38I shows that, acetone impurity in base stream is still far from the maximum limit (< 2%).

Consequences to safety/ environment

- Figure 5-38 shows that pressure still operates within the setpoint of 1.01 bar after 10% reduction of reflux flowrate. This pressure is still far from design pressure of 3 bars. The safety related problem does not exist due to 10% reduction of reflux flowrate. The same condition is also true for temperature changes in the column. It is shown from temperature profiles in figure 5-38B that pressure is still below design temperature of 150°C.
- Figure 5-38I shows that as 10% reduction of reflux flowrate reduces, acetone mass fraction in the base increases. This increasing trend of high acetone mass fraction in the base stream is an indication that reducing reflux flowrate will tend to decrease separation process in the top and thus accumulating acetone in the base.

20% and 30% reduction of reflux flowrate

Summary of control behaviour and consequences generated

Figure 5-39 shows results of investigation for disturbance due to 20% reduction of reflux flowrate. Whereas, Figure 5-40 shows the results of investigation for disturbance due to 30% reduction of reflux flowrate. These two figures tell that, the direction of response of pressure, level and temperature controllers for this disturbance have similar response as 10% reduction of reflux flowrate. While the behaviour of the response is similar, the different is only a matter of magnitude of the effects. Therefore, detail explanation follows the discussion of 10% reduction of reflux flowrate.

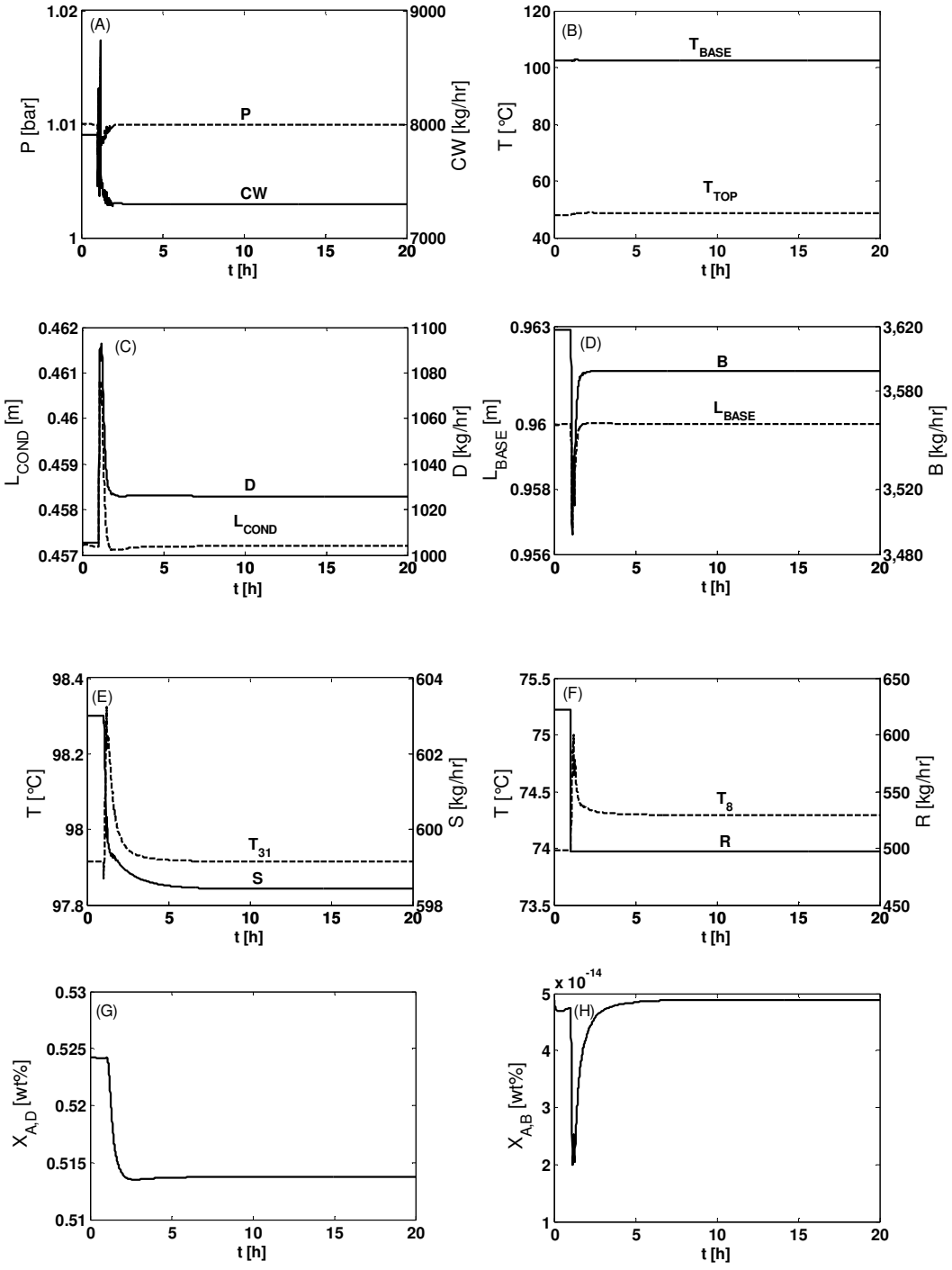


Figure 5-39. Investigation of effects due to 20% reduction of reflux flowrate

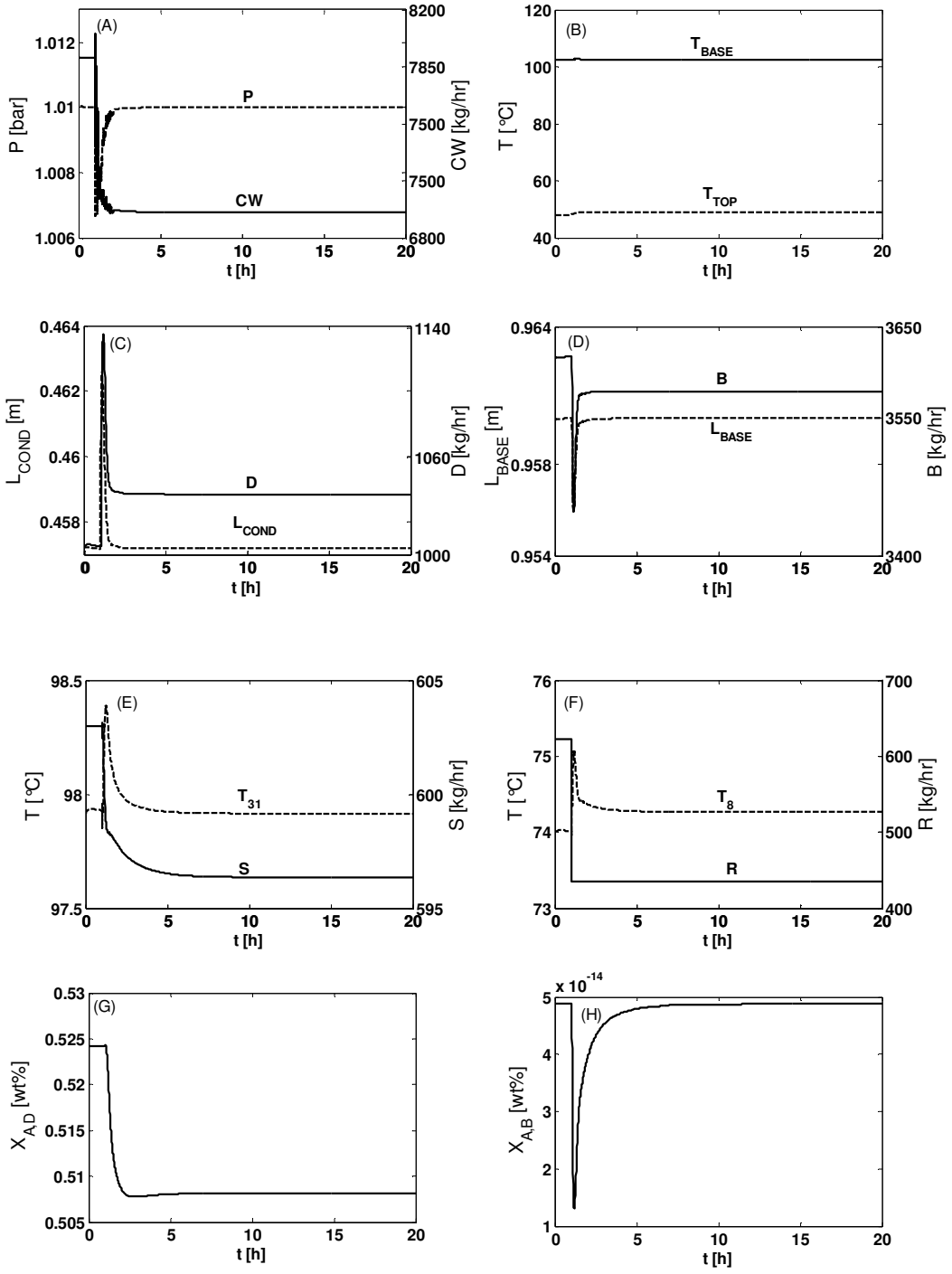


Figure 5-40. Investigation of effects due to 30% reduction of reflux flowrate

50% reduction of reflux flowrate

Summary of control behaviour and consequences generated

Figure 5-41 shows results of investigation due to 50% reduction of reflux flowrate. This figure tells that, the direction of response of pressure, level and temperature controllers for this disturbance have similar response as 10%, 20% and 30% reductions of steam flowrate. However, the reduction of 50% of reflux flowrate causes decreasing acetone mass fraction in distillate.

Figure 5-41C, 5-41I and 5-41F show the profile of product qualities. Figure 5-41C shows decreasing acetone mass fraction in distillate below the expected target (50 wt%). Therefore, the most important effect due to 50% reduction of steam flowrate is lower acetone concentration in distillate stream. It is reasonable since the lower reflux flowrate, the less effective is the distillation process.

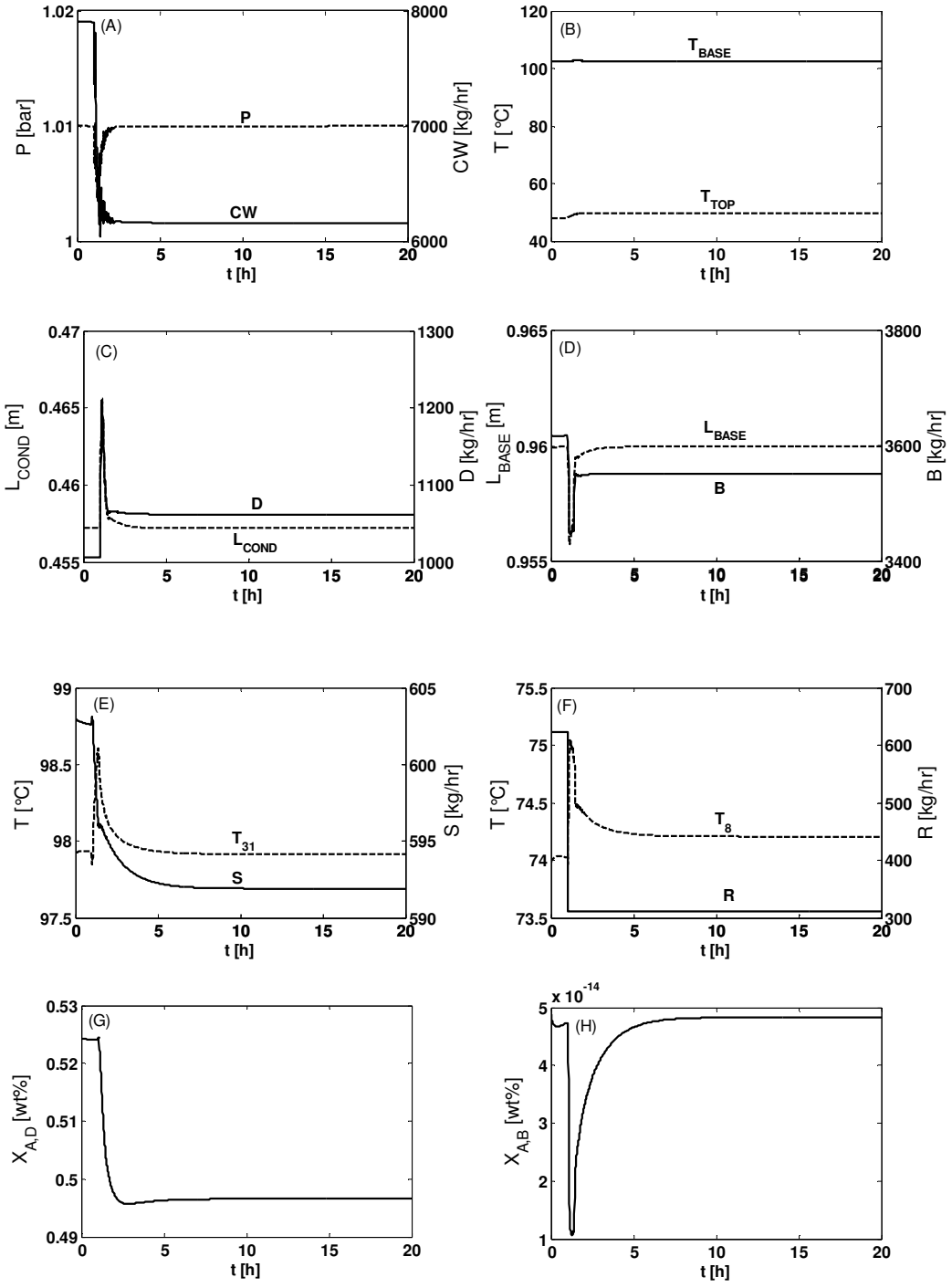


Figure 5-41. Investigation of effects due to 50% reduction of reflux flowrate

5.5.2.1.4 Sidestream disturbances

Each decision towards improvement must take into consideration its effects not only from merely conventional economic point of view, but its effects on environmental and safety as well. Therefore, this section will tell the role of dynamic simulation in this thesis to evaluate the effects of the design improvement under consideration (installation of sidestream).

According to Heikkila [63], the complexity will tend to increasing inherent safety index or, in other word, decreasing level of inherently safer design. Thus, challenging idea behind this simulation is waiting at answering some questions:

- how formal aspect of recent criteria can be applied at available design improvement?
- is it possible to adopt the existing criteria in the investigated case study which has a more complexity in design alternative than in the base case design?
- due to inappropriate usage of adopted criteria, should a new criteria for design improvement implemented in this study be introduced?

Effects of sidestream disturbance on control

To analyse possible consequences associated with the disturbance in sidestream, dynamic simulation is carried out. The evaluation is based on disturbances of –10%, -50% and +50% changes of sidestream flowrates. Figure 5-42 shows the simulation results of dynamic behaviour due to sidestream disturbance. Figure 5-42A shows that pressure is not affected by sidestream disturbance. 5-42B and 5-42C show that top and base temperature changes slightly (0.2 °C). This increased temperature is still far from design temperature (150°C). Level control remains the same indicating that top and bottom levels work properly in response to sidestream changes.

Effects of sidestream disturbance on products quality

The effects of sidestream disturbance is analysed based on changing –10%, -50% and +50% from initial design value of sidestream flowrate (450 kg/hr). Since disturbances on sidestream change mass flowrate in tray column, therefore the disturbance will also change bottom and top products flowrates. Figure 5-42A shows that as sidestream flowrate decreases, the amount of acetone in products decreases, and visa versa. Mass fraction of acetone is still within the expected target (> 50 wt%). Figure 5-42B and 5-42C show that as sidestream flowrate decreases or increases, the impurities of water in distillate product and acetone in base product will remain the same. Mass fractions of water and acetone are still below the limit (maximum of 10 %wt of water in distillate and 2 wt% of acetone in base). As sidestream flowrate changes, the amount of methanol in sidestream changes as well, as shown if figure 5-42D.

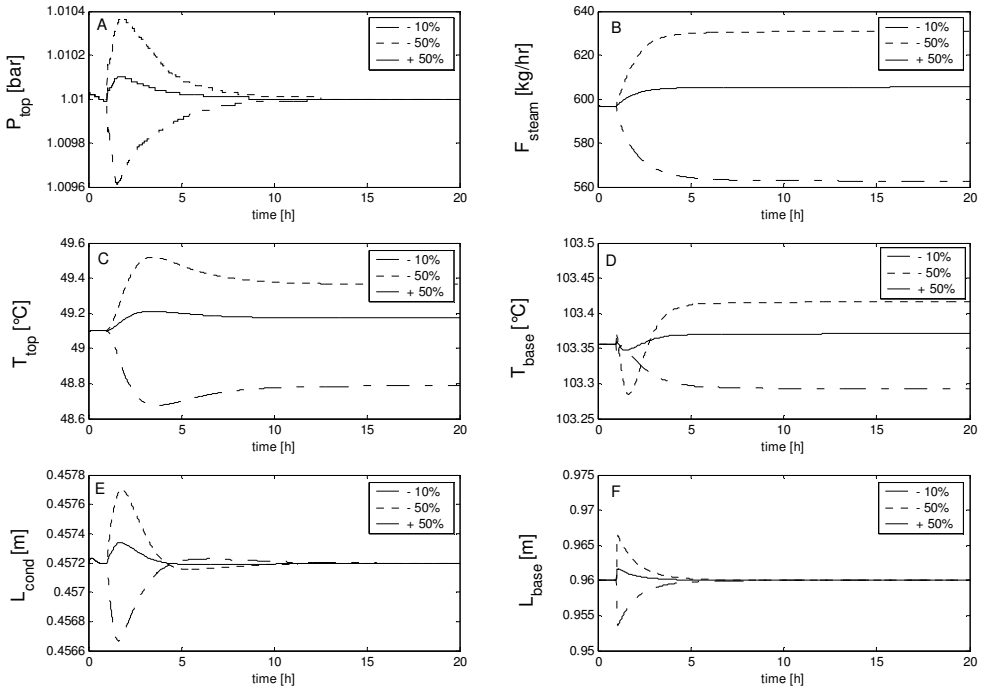


Figure 5-42. Investigation of the effects of sidestream disturbance on operating condition of sidestream distillation unit.

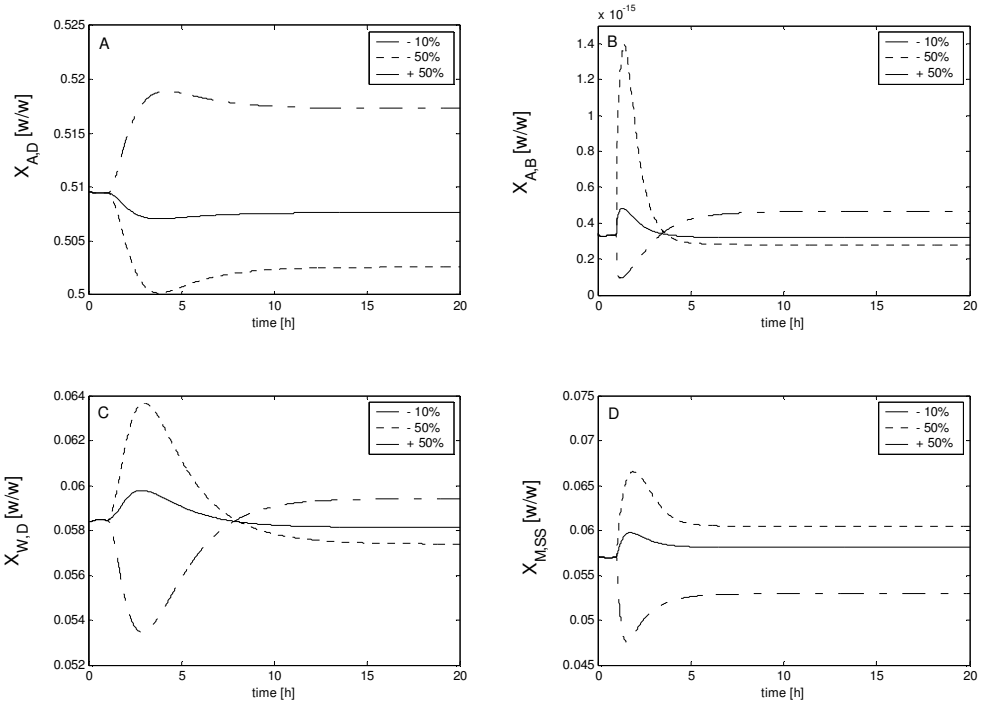


Figure 5-43. Investigation of the effects of sidestream disturbances on product quality.

Effects of sidestream loss

The effects of sidestream disturbance is analysed based on loss of 100% of sidestream flowrate. Since disturbance on sidestream changes mass balances in the column, so that it disturbs the mass balance in all trays hence changes base and top products. Figure 5-44A-D show that, as sidestream starts to empty, pressure, temperature and level column remain the same. Figure 5-45A and 5-45B show that as sidestream losses, bottom and distillate products flowrates increase. The increasing of bottom and distillate flowrates lead to increasing of steam and reflux flowrate (figure 5-45C and 5-45D). This findings give information that safety related problems associated with sidestream loss did not occur. As already mentioned, the only relevant changes due to sidestream are changes of distillate and bottom product which might no be a problem as long as the condenser capacity is big enough to liquefy the additional mass streams flowing to the condenser.

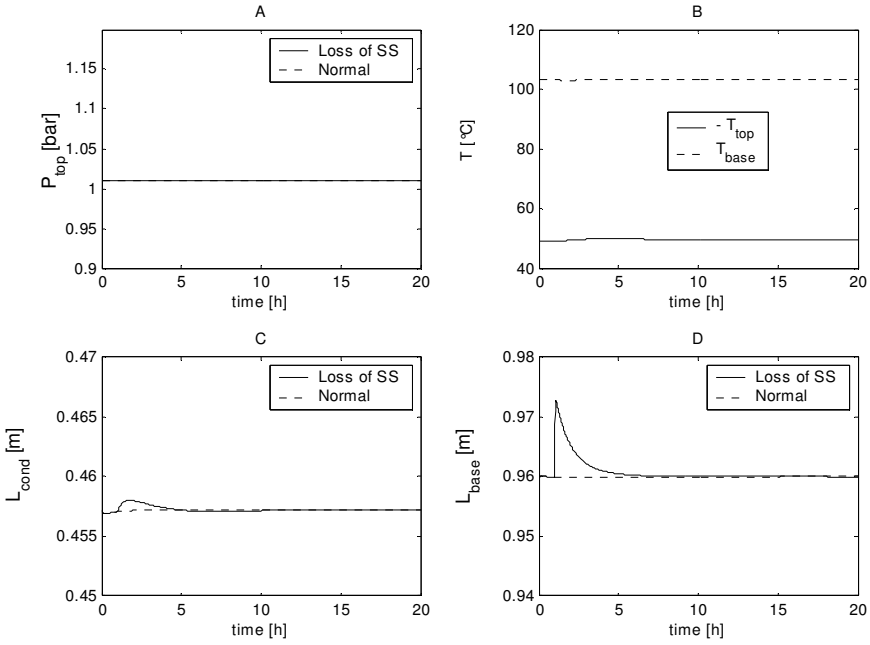


Figure 5-44. Effects of loss of sidestream flowrate on pressure, temperature and condenser and base levels

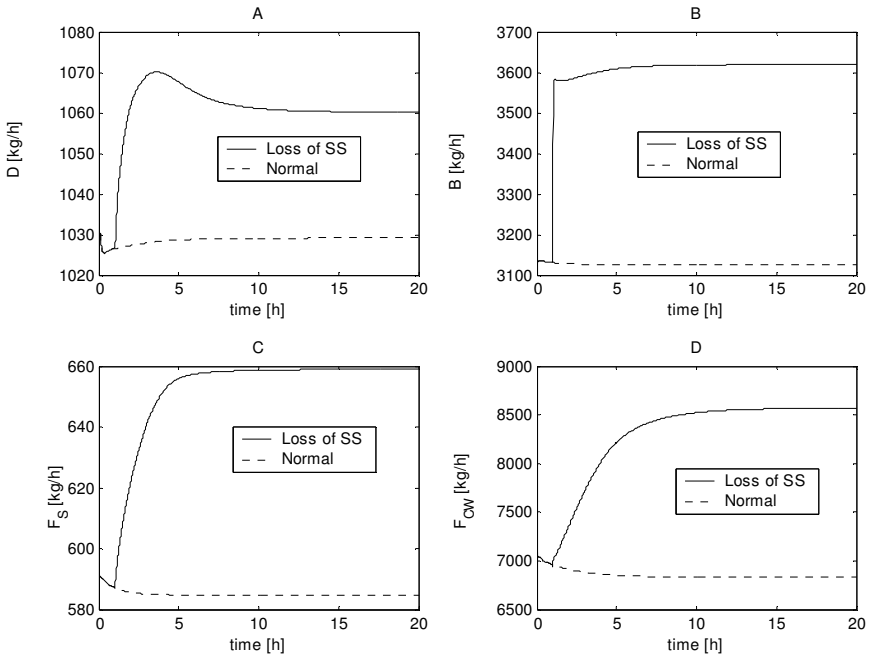


Figure 5-45. Effects of loss of sidestream flowrate on external flows (D,B,S and CW) of column. The sidestream design is used in this dynamic simulation.

5.5.3. Concluding remarks for this section

5.5.3.1. Conclusions

In order to stabilize the investigated unit operating at the expected operating condition and product qualities target, an optimum condition must be maintained. Some problems related to safety, product qualities and environment can occur due to particular disturbance when the unit is operated beyond the optimum condition. Therefore, dynamic simulation is used to investigate the behaviour of the investigated unit after particular disturbance was given. The optimisation work should give a condition that maintains the operation at the expected target. According to the results, set point value and controller location play important role in maintaining the stability of plant to response the disturbance.

From the results of dynamic simulation, effects generated due to disturbances of cooling water, reflux and steam have been investigated. The discussion includes control behaviour, product qualities and safety/environmental aspects.

Increasing pressure due to cooling water reduction will cause column temperature increases. Consequently, the controllers should work to minimize this increasing temperature. Bottom column controller will reduce steam flowrate thus temperature decreases. Reflux flowrate will decrease as steam flowrate decreases. However, in a condition when a high disturbance occurred, a higher driving force associated with the increased pressure occurred. As has been investigated in the simulation, the controller cannot compensate for the disturbance. This situation results in a non-normal condition where the dynamic behaviour did

not move to the expected direction. For this reason, a proper control system plays important role in distillation unit operation since it will maintain the process in a safe condition.

Disturbance of reflux or steam flowrates give the effects on material and energy balance on distillation unit. Especially, the change of mass balance due to steam will change obviously since steam is fed directly to the column. There is no effect on overpressure due to steam or reflux flowrate change. Change of reflux or steam flowrate will lead to change temperature of bottom and top column. Since the effect of temperature changes are still below the design temperature, thus safety related problem did not occur. The most important effect due to reflux and steam flowrate disturbances is decreasing of product qualities.

At the end, the results of dynamic simulation will notify the decision maker concerning the hazardous situation identified due plant disturbances. Some hazardous situation can be identified here such as overpressure (increased pressure), overheating (increased temperature), existence of vacuum and more pollutant releases. Other subsequent consequences such as flooding and weeping even not investigated directly in dynamic simulation but can be recognized from the existence of identified hazardous situation.

A column control philosophy that is either defective or unsuitable for the investigated is responsible for column instability. The instability can diversely affect the product purity, column capacity, economy and ease of operation. Instabilities are often transmitted to downstream or upstream units, or can amplify small disturbances. In extreme cases, instability can also lead to column damage or safety hazards.

5.5.3.2. Further analysis

There is a strong coupling between optimal values of the cooling water, reflux and steam flowrates as well as product qualities with set points temperature. Therefore, optimisation of the set points for temperature controllers is necessary to be considered as further analysis in order to achieve optimum condition (e.g. minimal total energy consumption) in the investigated distillation unit.

Another way to reduce operating cost of the investigated distillation unit is through employing correct control strategy. Accordingly, the investigation for other control structure will be of value for further analysis.

Another interesting aspect for further analysis is the improvement of product quality from sidestream. Since sidestream column produced only low purity, the investigation of energy with high purity sidestream with limit azeotropic system is an attractive topic for next improvement.

Since both set points are still conservative, therefore the effects of sidestream on stability should be also be investigated for further improvement.

5.6. Application of criteria to alternatives

After discussing fundamental aspects of distillation unit improvement, then this section will focus on the discussion of evaluation of criteria. The discussion will provide the application of basic assessment for each criterion in selecting the most suited design alternative. The simulation results from steady state and dynamic simulation are used for basic consideration in assessing all criteria. Those criteria considered in this section are economic, environment and safety criteria.

5.6.1. Economic criteria

This section explains the application of economic criteria assessment to design alternatives. With the use of simulation results, the assessment will be performed by mapping design variables into flowrates and process equipments specifications. Process equipment specification is used to estimate purchased equipment cost and flowrates are used to calculate recurring cash streams (either revenue or operating cost). Then, a common approach to obtain optimum process design is determined by minimising investment cost required and operating costs.

Operating cost is formulated as follows:

$$operating\ \cos t = F_S \cdot P_S + \dot{Q}_{COND} \cdot P_{COND} = F_S \cdot P_S + F_{CW} \cdot P_{CW} \qquad (5\text{-}12)$$

where CW and S represent cooling water and steam respectively. The annual cooling water use (F_{CW}) can be calculated as a function of the condenser duty generated from ASPEN Plus model simulation according to ASPEN utilities model as has been explained earlier in the ASPEN Plus process model (section 5.2). Total annualized cost will be used as objective function for evaluating economic criteria of design alternatives. Total Annualized Cost (TAC) will be used according to Brusis [21]:

$$TAC = Annualized\ investment\ cost + Operating\ cost \qquad (5\text{-}13)$$

The important utilities cost refers to Brusis [21] :

Cooling water cost : 0.05 €/t ; (298 K, 3 bar)
Steam cost : 10 €/t (low pressure steam)

For calculation of installation costs for improvement project, the calculation must consider the main investment cost regarding required equipments and instrumentation as well as costs for equipment construction (e.g. piping, instrumentation, engineering fees and contingency). In this thesis, the improvement cost calculation does not consider the costs associated with downtime for the improvement project.

For calculation of annualization factor, AF, Smith's method is used, with the discount cash flow, i=15% and operation process is 10 years.

$$AF = \frac{i \cdot (1+i)^N}{(1+i)^N - 1} = \frac{0.15 \cdot (1+0.15)^{10}}{(1+0.15)^{10} - 1} = 0.1993$$

Thus, from the calculation results in the annualization factor, AF = 0.1993.

The estimation of investment cost for improvement includes purchased equipment costs and modification cost for installation cost of sidestream in the base case design.

$$C_{TM} = C_{PE} + Modification\ cost \qquad (5\text{-}14)$$

where C_{PE} is purchased cost of equipment. Calculation of modification cost refers to Smith [123]:

$$C_{TM} = C_{PE,pump} + (C_{Mod} \cdot C_{PE,column}) \quad (5\text{-}15)$$

where C_{Mod} is cost factor of modification that refers to Smith [123].

Estimation of purchased cost of pump:

Pump cost can be estimated from cost calculator in online chemical engineering information (www.chesources.com and www.matche.com taken, in August 2006, with chemical engineering and plant index in 2006 is 766.2)
Equipment specification:

- Centrifugal pump type: Horizontal, ANSI, 1-stage
- Discharge pipe diameter: 4 inch
- Material: Cast Iron & API-610
- Seal type: packing
- Estimated purchased cost of a pump, $C_{PE,pump}$ = 5400 $

Estimation of modification cost in the investigated distillation unit:

- Equipment data: valve trays distillation column
- Known diameter, D_1= 0.5 m, size range: 0.5 – 4 m
- Base cost, C_B= $1.8.10^4$ $
- Cost exponent, M= 1.7
- For investigated unit, D_2 = 0.8 m
- Cost factor for distillation column improvement (adding sidestream) at particular tray according to Smith [123] (in this case study: at tray 22) : 0.1

Calculating purchases cost of column according to equation:

$$C_{PE,column} = C_B \cdot \left(\frac{D_2}{D_1}\right)^M$$

thus:

$$C_{PE,column} = 1.8 \cdot 10^4 \left(\frac{0.8}{0.5}\right)^{1.7} = 40020 \$$$

Then, according to equation 5-15, the calculation of modified cost of the column becomes:

$$C_{column,\ modified} = 5400 + (\ 0.1 \cdot 40020\ ) = 9420 \$$$

Annualized installation cost = AF x 9420 = 1790 $/a

Therefore, the investment cost for installing sidestream is 1790 $/a, whereas the investment cots for base design is zero (since no modification added).

Now, with the aid of utilities cost data mentioned above, the total operating costs are calculated in table 5-9 as follows:

Table 5-9. Comparison of operating costs between base case and sidestream design alternatives.

	Sidestream design alternative
Steam [kg/hr]	595
Cooling water [kg/hr]	7,102
Cooling water cost [$/a]	3,182
Steam cost [$/a]	53,285
Total operating cost [$/a]	**56,467**
	Base case design alternative
Steam [kg/hr]	603
Cooling water [kg/hr]	12,695
Cooling water cost [$/a]	5,687
Steam cost [$/a]	54,029
Total operating cost [$/a]	**59,716**

From those investment costs and operating costs above, the total annualized cost for both design alternatives can be calculated. Total annualized cost is the summation of investment costs and operating costs. Therefore, the calculation of total annualized cost for both design alternatives is as follows:

- TAC, base case = 59,716 + 0 = 59,716 $
- TAC, sidestream = 56,466 + 1790 = 58,256 $

From the calculation above, a trade off must be considered between investment cost and total operating cost. Comparison of all economic criteria for both design alternatives are shown in figure 5-46. From this figure, it is shown that total operating costs for sidestream design is lower than base design. Sidestream design requires investment cost, but the total annualized cost is still lower than base case design. The trade off in economic calculation is important to compromise between conflicting objectives in minimising cost of design alternatives. In this case study, total annualized cost is used as overall costs criteria to decide the best design alternative.

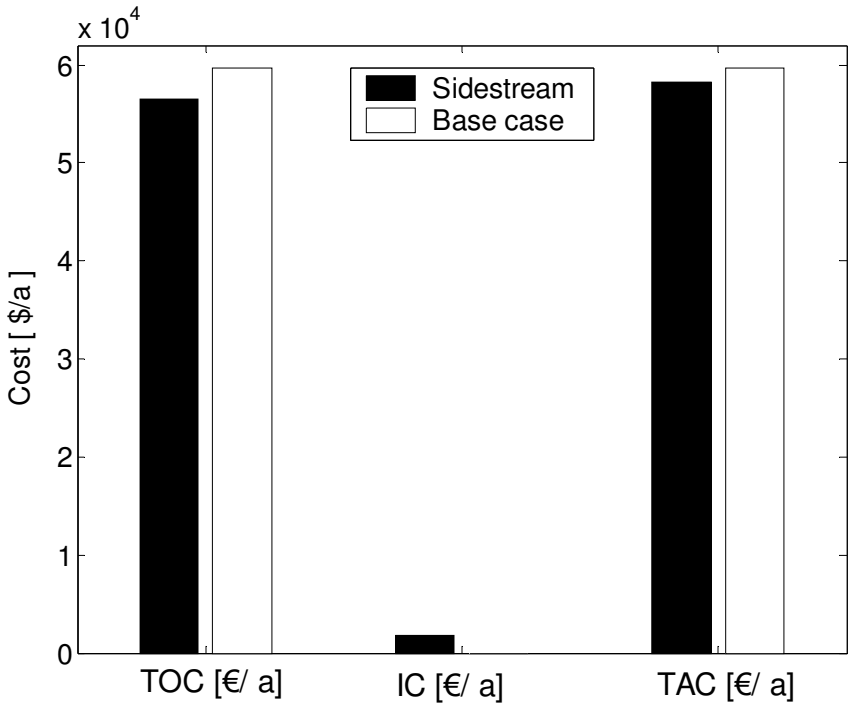


Figure 5-46. Comparison of economic criteria for sidestream and base case designs. TOC, IC and TAC refer to total operating cost, investment cost and total annualized cost respectively.

5.6.2. Environmental criteria

The evaluation of environmental criteria will rely on potential impact calculation. First, balance region for evaluating potential environmental impact is developed. Figure 5-47 shows the balance region for calculating impact balance around the investigated distillation unit. In this work, the relative importance of potential environmental impacts is determined under the guidelines of United States Environmental Protection Agency (US-EPA) [107].

Each chemical environmental impact potential is multiplied with its mass flow rate releases from distillation unit and sum these for all chemicals emitted, according to US-EPA equation:

$$I_j^* = \sum_{i=1}^{N} I_{j,i} \cdot m_i \qquad (5\text{-}16)$$

where I_j^* is the impact value for each category j, $I_{j,i}$ is the impact score of the emitted chemical i in the category j, m_i is the mass flowrate of the chemical i emitted. The data for potential environmental impact scores based on impact categories of each component are generated by WAR GUI and tabulated in the table 5-10 below.

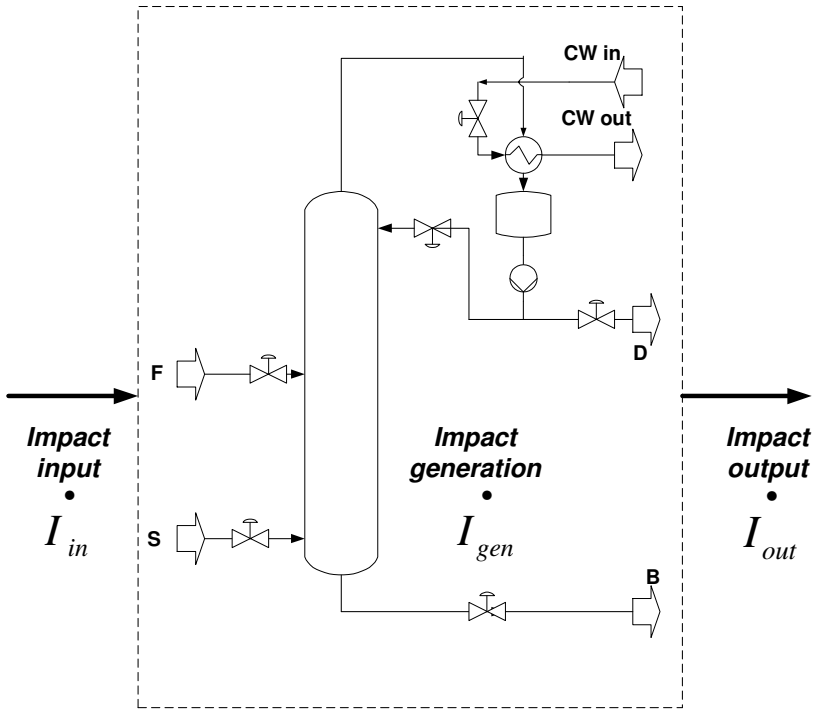


Figure 5-47. Impact balance of the investigated distillation unit.

Table 5-10. Potential impact scores for components of the investigated distillation unit.

Chemical	HTPI	HTPE	TTP	ATP	GWP	ODP	PCOP	AP
Methanol	0.0626	0.0011	0.0626	0	0	0	0.2462	0
Acetaldehyde	0.5332	0.0008	0.5332	0.0265	0	0	1.0547	0
Methyl formate	0.1696	0.0012	0.1696	0.0061	0	0	0	0
Ethanol	0.0499	0.0002	0.0499	0.0001	0	0	0.5364	0
Acetone	0.0608	0.0001	0.0608	0.0001	0	0	0.3562	0
Methyl acetate	0.1375	0.0005	0.1375	0.0023	0	0	0.05	0
Methyl ethyl ketone	0.1288	0.0005	0.1288	0.0003	0	0	0.9466	0
Ethyl acetate	0.0627	0.0002	0.0627	0.0039	0	0	0.4363	0
3-pentanone	0.1647	0.0004	0.1647	0.0006	0	0	0	0
Water	0	0	0	0	0	0	0	0
Acetic acid	0.1065	0.0117	0.1065	0.0107	0	0	0	0
Formic acid	0.3204	0.0326	0.3204	0.022	0	0	0	0
Propionic acid	0.1007	0.0098	0.1007	0.0141	0	0	0	0

The mass flowrates generated from steady state simulation as tabulated in table are multiplied by the scores of table 5-11 to create total potential environmental impact of each category for each design alternative.

Table 5-11. Potential environmental impacts of each stream in the investigated distillation unit

Impact categories	Stream input (Impact/kg)
HTPI	-1400
HTPE	-1820
TTP	-1410
ATP	-4760
GWP	0
ODP	0
PCOP	-3510
AP	0
TOTAL	-6410

Figure 5-48 shows comparison of potential environmental impact for both design alternatives. From this figure, sidestream column is more superior (less potential environmental impacts) in terms of HTTPI (human toxicity potential by ingestion), HTPE (human toxicity potential by either inhalation or dermal exposure), TTP (terrestrial toxicity potential), aquatic toxicity potential) and PCOP (photochemical oxidation potential). The last potential environmental impact is most probably determined by the amount of methanol. The more methanol can be recovered, the less PCOP.

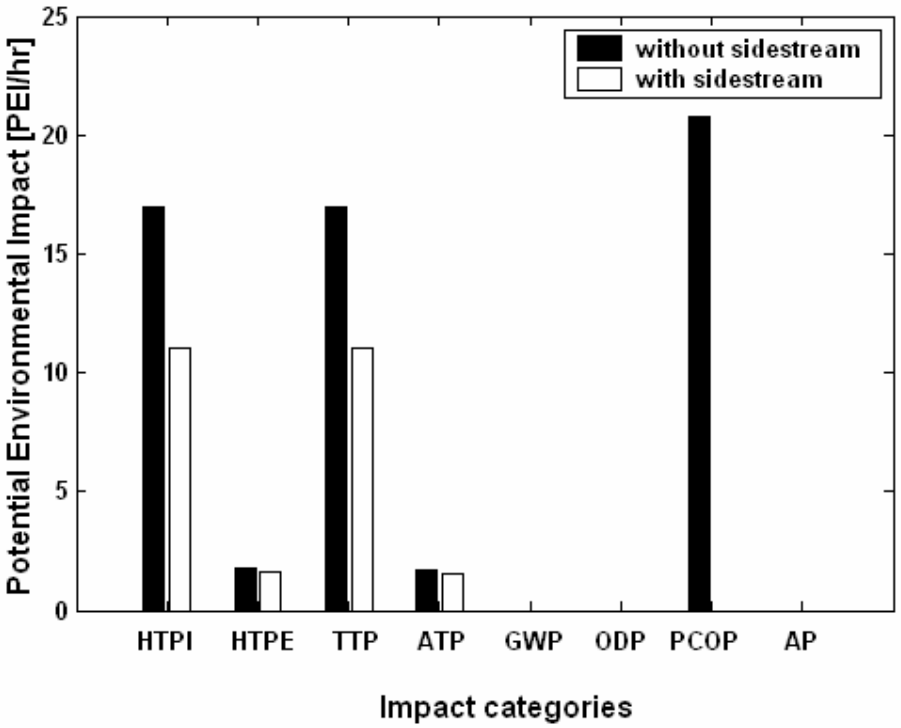


Figure 5-48. Comparison of potential impacts between both alternatives. HTTPI (human toxicity potential by ingestion), HTPE (human toxicity potential by either inhalation or dermal exposure), TTP (terrestrial toxicity potential), ATP (aquatic toxicity potential) GWP (Global Warming Potential), ODP (Ozone Depletion Potential), PCOP (photochemical oxidation potential) and AP (Acidification Potential).

The assessment methodology using environmental impact criteria is capable of designing and selecting the process with minimal environmental impact at a desired economic performance.

However, different community or regulation tends to particular single criteria (e.g. toxic release criteria) must be focused or concerned as the highest priority over the others within the evaluation of chemical process design. The reason for prioritising particular environmental impact is that the components included in distillation unit in chemical industry is responsible for a large fraction of hazardous materials releases to the environment that cause detrimental effects to the people around the location. In addition, public is more concerned about direct chemical's effect that distillation unit might cause to the people.

Unfortunately, the information regarding the potential environmental impact of chemical in the environment is incomplete and imprecise, as already explained in chapter 4. Nevertheless, the information available should be used maximally to support efforts to improve the environmental performance of products and processes in distillation unit. Thus, the supporting tools for designing and improving distillation unit can be broadened by assessing and recognising the main drives of potential environmental impacts in distillation unit. Further, the work in this field should result in unit indicators for distillation unit design evaluation.

5.6.3. Safety criteria

5.6.3.1. Risk potential

As explained in chapter 3, in order to improve the quality of decision making process for improving safety performance, the risk potential matrix is used as decision making approach to improve plant safety performance. The preliminary work for the assessment of risk potential in this investigate system has been performed [134]. However, the discussion to compare both design alternatives based on risk potential assessment will not be integrated here since the results from dynamic simulation showed that both design alternatives have the same bases in risk analysis potential. Even sidestream has one stream more than base case design, but the results of dynamic simulation explained that the loss of sidestream flowrate did not generate a new hazard situation. Based on these reasons, the risk potential for both alternatives is assumed equivalent.

5.6.3.2. Inherent safety

The inherent safety assessment of design alternative aims to point out the most vulnerable point in the design. The correlation of total inherent safety of a design or process is formulated as follow:

$$I_{TI} = I_{CI} + I_{PI} \qquad (5\text{-}17)$$

where I_{TI}, I_{CI} and I_{PI} represent total score of inherent safety index, inherent safety subindex of chemical used and inherent safety subindex for process design or structure.

Since changing distillation unit design do not consider reactivity, flammability, explosiveness, and corrosiveness of materials which compose the inherent safety subindex for chemical used, thus the first term in the equation above can be neglected. Thus, the inherent safety relies only on the process index associated with equipment or process structure design and operating parameters. Equipment design safety tries to measure the possibility that a piece of equipment or availability of a stream in a plant design might cause unsafe condition and provides opportunities for error, thus the inherent safety principle of "simplification" will be considered for evaluating the inherent safety subindex of process design.

Example of the evaluation of inherent safety score for distillation as a unit within a whole chemical process is tabulated in table 5-12. It is obvious that the score is useful for comparison with another unit and regardless comparison changing distillation design itself. Therefore, for comparing one alternative with another, the inherent safety score uses the score for process structure evaluation. This process structure considers the number of streams involved and the number of control loops used. The less the number, the higher inherently safety condition of the design. Table 5-13 below shows a comparison for basic evaluation in comparing the design alternatives in this work. It is obvious from that table 5-13 that the base case design without sidestream gives inherently safer design with regard to process structure selection than the design with sidestream.

Table 5-12. A comparison for inherent safety score regarding process structure evaluation

Inherent safety sub-criteria	**Design alternatives**	
	Base case design	**Sidestream design**
Number of streams involved	4	5
Number of control loops	5	6

Table 5-13. Application of total inherent safety index in the case study. The calculation refers to Heikkilä [63].

Inherent safety criteria	**Description**	**Score for BS**	**Score for SS**
Chemical inherent safety index			
Heat of main reaction	No reaction	0	0
Heat of side reaction, max	No side reactions	0	0
Flammibility, explosiveness, toxicity	Maximum sum for acetic acid	7	7
Corrosiveness	Stainless steel	2	2
		∑ = 9	∑ = 9
Process inherent safety index			
Inventory	4. t/h	3	3
Process temperature, max	110° C	2	2
Process pressure, max	2 bar	0	0
Equipment	Distillation tower	1	1
Index of structure	Number of control loops and streams	9	11
		∑=15	∑=17
Total inherent safety index		**24**	**26**

Note: BS: base design; SS: sidestream design.

5.7. Multicriteria decision making analysis

5.7.1. Qualitative analysis

The results from dynamic simulation will provide an insight how to operate the investigated distillation unit to meet the target. Unfortunately, previous researches of dynamic behaviour have been limited in investigating the control configuration stability when the disturbance occurred without considering environmental effects. For example, Luyben [104] has investigated dynamic disadvantages for operating inherently safer distillation unit. Therefore, this study will broaden the scope of investigation into safety and environmental effects due to disturbances.

For choosing the best options amongst alternatives in this case study, a multicriteria decision making analysis must be made. The analysis in multicriteria decision making must take into consideration possible conflicting objectives (e.g. improving one criterion but worsening other criteria). A qualitative analysis by Palaniappan, Srinivasan and Halim [112] is the simple way to address the conflicting objectives in plant operation. This article gives a framework for qualitative analysis in addressing environmental, safety and economic issues. Some issues that are relevant for the investigated column are presented for the purpose of illustration, as shown in table 5-14.

Table 5-14. Key words of conflicting objectives between operability and safety objectives in the investigated distillation unit

Key words	Operability issues	Safety issues
Increase or decrease pressure	Increase pressure to increase separation performance and reduce waste	Reduce pressure to reduce risk and improve inherently safer index
Increase or decrease pressure	Increase pressure to reduce cooling water	Reduce pressure to reduce risk and add cooling water to increase distillate
Increase or decrease cooling water	Reduce cooling water to optimise operating condition (find optimum pressure or temperature)	Increase cooling water to increase distillate
Improve design/structure or simplify design	Add sidestream to increase product quality and reduce waste stream	Simplify the design to improve system reliability and inherent safety
Apply heat integrated or simplify	Improve design for heat integrated design and thus reduce energy demand	Simplify the design to improve system reliability and inherent safety

According to table above, there will be conflicting objectives in operating the investigated distillation unit when particular policy will be decided to increase product quality and produce less waste, but unfortunately, violates inherently safer design principle. For example, in order to improve separation process performance and reduce waste, a policy to implement higher pressure could be applied. However, this decision will violate inherently safer principle to maintain pressure.

It is shown from the previous results that poor dynamics behaviour can result in more nonseparated components dropping out the bottom of the column and subsequently flowing

into wastewater stream. With regard to product quality issues, part of the disturbance implications relate to less quality of product or the off-grade product. From the view point of pollution prevention, this waste release into environment is recognized as detrimental material released from the investigated distillation unit.

The worst case of this problem is that the plant will be shut down to avoid producing large amounts of bad product. According to dynamic simulation results, an example of the off-specification product can be found in a case of 50% reduction of steam flowrate. Then, if this operation needs the plant to be started up again, there will be higher risk phase of plant operation. From this reason, there is a significant interaction between environmental problems and safety.

5.7.2. Application of analytical hierarchy process

To decide the best design alternative, the analytic hierarchy process (AHP) will be used for decision making methodology in this thesis. The alternatives of sidestream and base case design are deduced and three criteria are defined. All criterion will be assigned for each alternative. For the illustration of states, relationships, alternatives, preferences, and interrelation between them, a hierarchy of multicriteria decision is constructed, as shown in figure 5-49 below. This hierarchy is composed of three types of node, namely objective node (which represent overall objective of distillation unit improvement), chance node (consists of criteria and subcriteria) and decision node (consists of design alternatives).

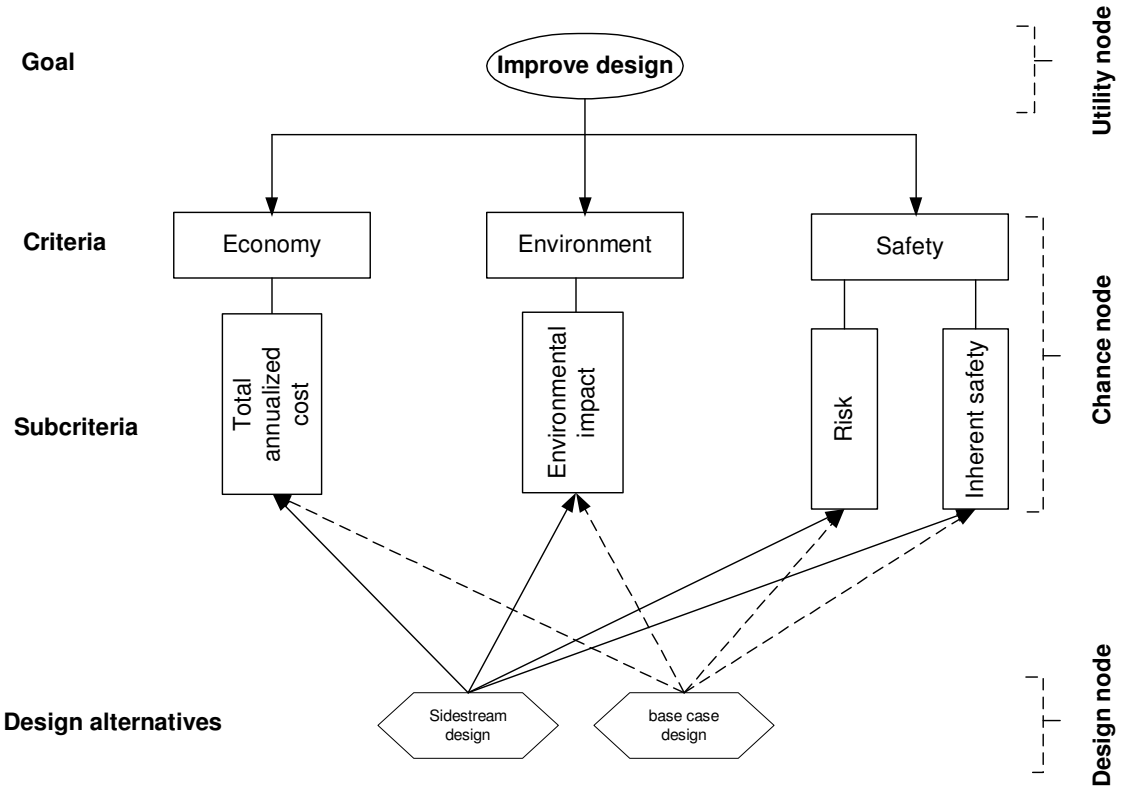


Figure 5-49. Multicriteria Decision Making (MCDM) hierarchy for the case study

As has been explained in the preceding section, the goal of improvement for the investigated distillation unit are:

- Minimise economy criteria: improving economy performance through minimising total annualized cost.
- Minimise safety criteria: improving safety through minimising safety index calculated
- Minimise environment criteria: improving environmental performance through minimising potential environmental impact

The goal of minimization performance of all criteria in this case study has a consequence that the lower score value has a better performance.

5.7.2.1. Synthesis of criteria matrix

The first step in multicriteria decision making using AHP method is the synthesis step. The main task in this step shall a creation of pairwise comparison matrix and relative weights of design alternatives with respect to each criterion [115]. The aim of this section is to develop a standard decision table with m criteria and n alternatives, as shown in table below. Let C_1, …, C_m and A_1, …, A_n denote the criteria and alternatives respectively. In the table each rows belongs to each criterion and each column describes the performance of an alternative. The score a_{ij} describes the performance of alternative A_j against criterion C_i.

		x_1			x_n
		A_1	...	...	A_n
w_1	C_1	a_{11}	...	...	a_{m1}
	.	.		.	.
	.	.	...	.	.
	.	.		.	.
w_n	C_m	a_{m1}	...	...	a_{mn}

Figure 5-50**.** The illustration of decision table needed in this case study.

This matrix acts as comparative judgment where decision maker can compare any two criteria belonging to each improvement option. The input data for comparative judgments are provided in the preceding section. This data is used to derive weights and priorities. All comparative judgement matrices are described according to each criterion.

The next step is the pairwise comparison of the design alternative. This pairwise comparison is developed to quantify how well the decision maker satisfies to take one design alternative and relate quantitative drawbacks of that alternative compared to another alternative. This pairwise comparison is done by assigning a weight between 1 (equal importance) to 9 (absolutely more important) to the more preference design alternative, and the reciprocal of this value is then assigned to the other alternative. The basic for calculation of the weight is from the values resulted from evaluation criteria.

Pairwise comparison among n criteria lead to an approximation of each $a_{ij} = \frac{w_i}{w_j}$ which is the ratio of criteria i to element j. The estimated weight vector is found by solivng the following eigenvector problem:

$$A \cdot w = \lambda_{\max} \cdot w \qquad (5\text{-}18)$$

where A consists of a_{ij}'s, and λ_{max} is the principal eigenvalue of A. Matrix A can be written out more fully as follows:

	A_1	A_2	...	A_n
A_1	$\frac{w_1}{w_1}$	$\frac{w_1}{w_2}$	...	$\frac{w_1}{w_n}$
A_2	$\frac{w_2}{w_1}$	$\frac{w_2}{w_2}$	...	$\frac{w_2}{w_n}$
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.
A_n	$\frac{w_n}{w_1}$	$\frac{w_n}{w_2}$	...	$\frac{w_n}{w_n}$

$$\begin{bmatrix} w_1 \\ w_2 \\ . \\ . \\ . \\ w_n \end{bmatrix} = n \begin{bmatrix} w_1 \\ w_2 \\ . \\ . \\ . \\ w_n \end{bmatrix}$$

or

	A_1	A_2	...	A_n
A_1	1	a_{12}	...	a_{1n}
A_2	$\frac{1}{a_{12}}$	1	...	a_{2n}
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.
A_n	$\frac{1}{a_{1n}}$	$\frac{1}{a_{2n}}$	...	1

$$\begin{bmatrix} w_1 \\ w_2 \\ . \\ . \\ . \\ w_n \end{bmatrix} = \lambda_{\max} \begin{bmatrix} w_1 \\ w_2 \\ . \\ . \\ . \\ w_n \end{bmatrix}$$

In order to calculate the *w* vector (also called eigenvector), each column of *A* is first normalized and then arranged over its row. This vector is to find relative importance of its element.

As pointed earlier in dynamic simulations, the relative weights contained in table are indicative of the components' importance with respect to the overall goal of improving performance of the investigated distillation unit. These relative weights can be used to denote either the priority rank or magnitude of importance of each component. The consideration of priority ranking is based on following reasons:

- Energy consumption and product qualities are critical to be affected by disturbances. Steam and cooling water consumptions are the most important aspects that affect the overall economic cost performance. These aspects are critical when the disturbance occurred.
- Safety is the second affected aspect that critical due to the occurrence of disturbance. Safety aspect is affected most by cooling water reduction which causes overpressure or high temperature. The effect of safety problems can cause more serious than environmental problems.
- Environmental releases due to disturbances are the least critical aspect since the magnitude of the effects is less critical. The results from dynamic simulation also show that distillation unit will not generate environmental problems with low disturbance level.

As a consistency of those relationships, the weighting value of economic criteria is higher than weighting values of safety and environmental criteria, while the weighting value of safety will be higher than the weighting value of environmental criteria but lower than weighting value of economic criteria. From these reasons, the following priority ranking can be formulated as follows:

$$w_{economic} > w_{safety} > w_{environment} \quad (5\text{-}19)$$

where w is weighting factor for criteria. It means that, economic criteria outranks (or more important) over safety and environment criteria, while safety criteria outranks over environmental criteria. Next, this outranking relationship will be used as the basic of weighting values of each alternative. The values will use the pairwise comparison scale according to the methodology of analytical hierarchy process (AHP) (see chapter 4). Since the priority of each criteria considered to be between moderately more important and equally important (value of 2 based on AHP methodology), therefore each outranking level has a weight of 1 weighting value higher. It means, economic, safety and environmental criteria will have a weighting value of 3, 2 and 1, respectively. These values will be used to accomplish pairwise wise comparison matrix with respect to criteria, as shown in table 5-16.

Table 5-15. Matrix of criteria comparison between base case and sidestream designs based on analytical hierarchical process

Criteria	Values		Normalized	
	Base case	Sidestream	Base case	Sidestream
Economic	59,716	58,256	0.51	0.49
Safety	24	26	0.48	0.52
Environment	63.7	27.1	0.70	0.30
Average			0.56	0.44

The average values provide the preferences of decision maker for each design alternatives with respect three criteria. Now, the following table, table 5-16, represents a pairwise comparison of each criteria.

Table 5-16. Pairwise comparison matrix and its normalized values

Pairwise comparison

	Economy	Safety	Environment
Economy	1	2	3
Safety	0.5	1	2
Environment	0.33	0.33	0.33
Sum	1.83	3.33	5.33

Normalized values of pairwise comparison

Normalized				SUM	AVERAGE
	Economy	Safety	Environment		
Economy	0.55	0.60	0.56	1.71	0.57
Safety	0.27	0.30	0.38	0.95	0.32
Environment	0.18	0.10	0.06	0.34	0.11

Table 5-16 above shows a decision table to decide a rank of importance. This table ranks a relative importance for the improvement options of distillation unit operation from the highest priority criteria into the least priority. The average weights on the last column in the table of normalized comparison judgement matrix shows that economic consideration for improving distillation column should be considered in a preference of 57% importance, followed by safety consideration with 32 %, as well as 11 % preference for environmental consideration. These average values (the vector of last right hand column of normalized comparison judgment matrix) provide the preferences of decision maker for both design alternatives according to three criteria. Therefore, there are three preference vectors that can be summarised into a composite relative weight of overall criteria. These composite relative weights will give criteria rankings for deciding the most promising alternatives.

5.7.2.2. Rating of design alternative

The final step in the AHP is to combine the average normalised design alternative ratings (table 5-15) with the average normalised criterion weights (table 5-16), to produce an overall rating for each design alternative, i.e. the extent to which design alternative satisfy the criteria is weighted according to the relative importance of the criteria. This is done as follows:

$$a_j = \sum_i (w_i \cdot k_{ij}) \qquad (5\text{-}20)$$

where:

a_j = overall relative rating for design alternative j

w_i = average normalised weight for criterion i

k_{ij} = average normalised rating for design alternative j with respect to criterion i

For the investigated distillation unit with base case (BC) and sidestream (SS) design alternatives and considers three improvement criteria (economic safety and environmental criteria), the equation above can be derived as follows:

$$a_{BC} = (w_{economic} \cdot k_{economic,BC}) + (w_{environment} \cdot k_{environment,BC}) + (w_{safety} \cdot k_{safety,BC}) \quad (5\text{-}21)$$

$$a_{SS} = (w_{economic} \cdot k_{economic,SS}) + (w_{environment} \cdot k_{environmnet,SS}) + (w_{safety} \cdot k_{safety,SS}) \quad (5\text{-}22)$$

Rearranging the results of composite judgment matrix from table 5-15 and table 5-16, following figure can be constructed to represent all the values required to calculate overall relative rating for design alternative according to equations 5-21 and 5-22 above.

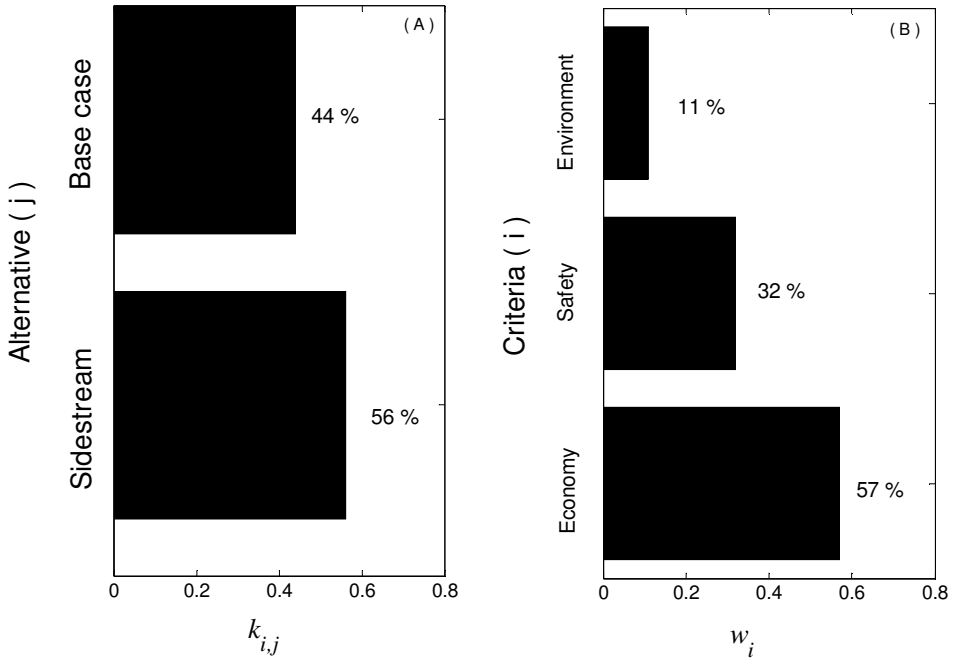


Figure 5-51. Weighted head to head between base case and sidestream design. (A): priorities with respect to alternatives, (B): priorities with respect to criteria

From figure 5-51 above, a matrix of weights for design alternatives preference is obtained. The results shows that design alternative with sidestream will be chosen in order to improve distillation design with regard to all three criteria. The matrix below:

$$\begin{vmatrix} 44\ \% & 56\ \% \end{vmatrix}$$

gives decision maker a preference in 56 % to choose sidestream distillation as the improved design, whereas only 44 % to keep base case design with the particular operating condition mentioned in the simulation. The resume of both consideration can be summed up into one graphical representative of aggregate results, as shown in figure 5-52.

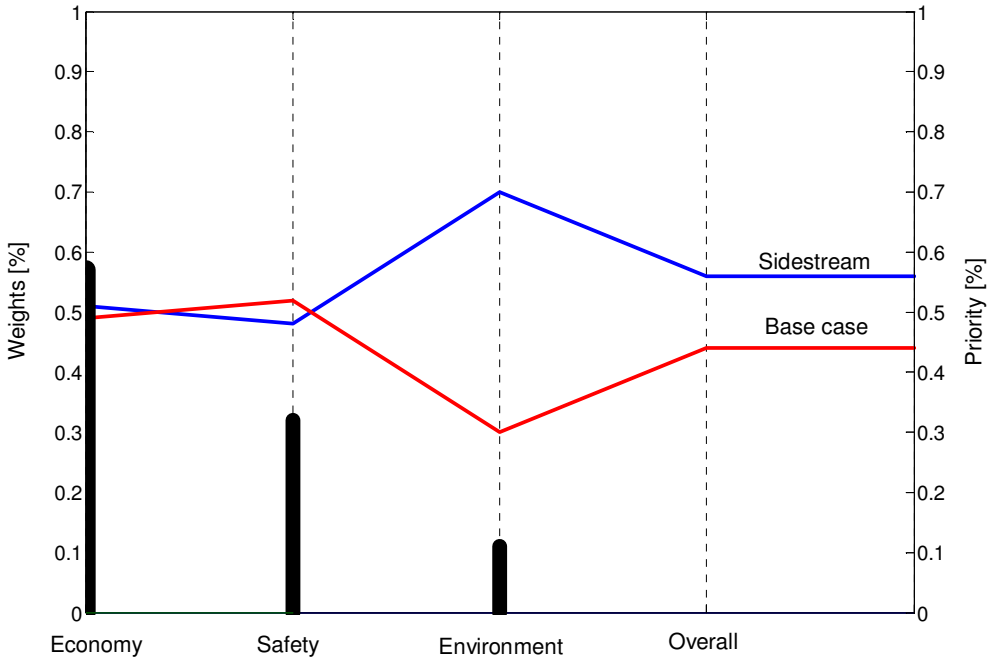


Figure 5-52**.** Graphical representative of aggregate results

The improvement objective for each criteria are represented by verticals bars, and the improvement option as alternatives are indicated as horizontal line graphs. The intersection of an alternative line graph and a vertical objective line indicate the priority of the options for the given criteria, as read from the right axis. The priority weight on an impact is represented by the height of bar and read from the left axis. The overall priority of each option is represented on the overall line and read from the right axis.

6. Conclusions and Outlook

Optimisation and improvement in distillation technology is a demanding task and has a decisive impact on overall plant performance. It is very often that, a large number of alternatives with different structure design an process alternatives of distillation technology can be found to satisfy the demanded criteria of improvement. Those criteria that are in increasing awareness to be fulfilled in distillation technology are safety, environment and economy. Therefore, a systematic method for the improvement of distillation unit is of the considerable interest in order to achieve the improvement objectives with regard to economic, environmental and safety criteria. The fundamental task in integrated improvement of distillation unit in this thesis is a detail evaluation of economic, environmental and safety criteria for each design alternatives. Then, a decision of the best design alternatives for this integrated improvement strategy are proposed based on a framework of multi criteria decision making analysis.

6.1. Summary

A general overview of the application of computer aided design and systematic framework for conducting environmental conscious design of chemical processes is straight forwarded. In this work, process simulation tool is used to facilitate multicriteria decision making for evaluation of economic, environmental and safety objectives in distillation unit. The use of steady state and dynamic simulation in this thesis has given a full understanding of inherently safer design characteristics of distillation unit. The information provided from distillation unit simulation can be of value and essential for the selection of the best process alternatives.

The attractiveness of existing acetone recovery column as the investigated case study in this thesis is used to demonstrate environmental, safety and economic evaluation in distillation unit improvement. With the task of improvement design to improve acetone recovery as well as minimum waste and steam requirement, design alternatives are created. Design alternatives generated should effectively control product quality, minimise waste and maintain plant safely. Since the economic criterion is often too coarse to discriminate the best alternatives and sacrifices other important criteria, thus, the criteria for improvement are extended and integrated in this thesis, namely safety, environmental and economic.

Application of the proposed methodology to the case study for the improvement of environmental performance shows the analysis technique to determine causes and sources of the environmental impact in the investigated distillation unit. Environmental assessment relied on the information from heat and mass balance generated by process simulation. Then, the evaluation of potential environmental impact (PEI) is performed based on waste reduction algorithm. The improved design shows that PEI can be reduced.

The focus on recent safety assessment method in this case study is to identify the trends of growing malfunction sources in distillation unit. The malfunction condition is assumed as a situation where severe disturbance occurred. Using dynamic modelling of distillation column behaviour during operational disturbances, the effect of such disturbances can be systematically characterized. Then, a combination of the dynamic modelling of distillation column behaviour during disturbance condition or non-standard operation with the failure mode and safety analysis (FMEA) will give a deeper understanding of system safety. The valuation of frequency and consequence associated with particular disturbance has been defined and the potential index (RPI) matrix has been developed to reveal potential risk associated with those disturbances. The results could then be used for decision making in the

development of new design regulations that would help to achieve hazard free operation in distillation technology.

In deciding the best options amongst available alternatives, a multicriteria decision making analysis has been made. The method of multicriteria decision making must take into consideration possible conflicting objectives available between inherently safer plant and waste minimisation, since inherently safer plant might not be less pollutant generated, or visa versa. An analytic hierarchy process has been used in order to support decision upon the criteria for selection, rate the relative importance of the criteria and its advantages/ disadvantages as well as to combine the rankings to obtain an overall rating for each potential choice. The decision developed can support decision maker to decide upon the best criteria between available alternatives. Correspondingly, an increased probability of finding the best design alternative which satisfies all required criteria is to be expected. Despite the rather arbitrary aspects of the procedure, however, it can provide useful insight into the tradeoffs embedded in a decision making problem of improvement task in distillation unit.

6.2. Further research

The results presented in this thesis show that the conceptual integrated improvement of distillation unit using multicriteria decision making analysis is an effective tool for decision support tool to find the best design alternative considering environmental, economic and safety in distillation technology. Nevertheless, several opportunities for improvements and extensions with regard to computational aspects, application to extended and even larger scale alternatives as well as development of energy – environmental based model can be perceived. Following section provides a summary of promising leads.

Improvement on the computation of the multiobjective optimisation. Advanced optimisation programming like evolutionary algorithm has emerged as important platforms for high performance multiobjective optimisation computing. The development of powerful, more effective and efficient computational program on conceptual optimisation is a challenging endeavour. A multiobjective optimisation framework in which process, plant and product designs are combined together and with process operability, mass and energy intensity, and environmental impacts might be included in the objective function set and is developed for further optimisation level using Aspen Plus simulator. An example of a trade-off strategy in process improvement in distillation column considering environmental and economic criteria has been performed by Hostrup, Harper , Gani [73] and Smith [124]. According to their work, genetic algorithm is found robust and able to adequately handle the multiobjective nature of the two ore more criteria in distillation columns.

Extended implementation on large scale of alternatives. This thesis focused on distillation unit, with sidestream as a design alternative. The promising results and its capability make it desirable to extend this approach to a larger set unit of design and process alternatives of distillation unit. Hence, improvements projects in this area should be continued in order to widen the scope of the design framework. The application of multicriteria optimisation could be an interesting especially for new field on hybrid process and heat integrated design that attracted researchers nowadays due to their capabilities in saving energy, even though some of them show some restrictions.

Decision support tools for the generation of promising process alternatives. Due to the large number of considerations involved in many decisions, decision support systems should also be developed to assist decision makers in considering the implications of various courses of innovation in distillation technology. Develop a method that allow the rapid identification of opportunities to integrate processes. The development of "an interactive, flexible, and adaptable computer-based information system for design, simulation, analysis in distillation technology. It utilizes data, provides an easy-to-use interface, and allows for the decision maker's own insights.

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Appendix

A.1. Column dimension for case study

The column serve as a guide for the evaluation of the column hydrodynamics. These values are shown in table below:

Table A.2.1. Tray design parameters

Design Parameters	
Number of plates	35
Type of plate	Valve
Liquor path	Single cross flow

Table A.2.2. Column internal configuration

Parameter	Unit	Tray 1 - 15	Tray 16 – 35
Internal column diameter	m	2	2
Tray spacing	m	0.300	0.300
Exit weir length	m	0.576	0.036
Exit weir height	m	0.030	0.030
Downcomer exit length	m	plain	Notched
Downcomer area	m^2	0.0494	0.0117
Downcomer clearance	m	0.030	0.030
Active area	m^2	0.3939	0.4693
Hole diameter	m	46	55
Valve per tray	-	46	55
Valve pitch	m	0.074	0.080

Table A.2.3. Valve design parameters

Parameters	Unit	Value
Valve diameter	m	0.048
Equivalent diameter minimum	m	0.0032
Equivalent diameter maximum	m	0.017
Minimum vertical travel	m	0.0016
Maximum vertical velocity	m	0.009
Valve thickness	m	0.0015
Valve mass	kg	0.022
Valve material density	kg/m^3	8025.3

A.2. Determining thermodynamic model in process simulators

A.2.1. Thermodynamic Models in ASPEN Plus

The operations of units predicted with ASPEN Plus are only trustworthy if the thermodynamic model used is applicable. Table 4.1. below gives an overview of thermodynamic models considered in ASPEN Plus. The choice of suitable thermodynamic model follows the decision tree as depicted in figure below.

Table A.4.0-1.Thermodynamic models in ASPEN Plus

Equation-of-State Models (EOS)	Activity Coefficient Models
Benedict-Webb-Rubin-Lee-Starling	Electrolyte NRTL
Hayden-O'Connell[1]	Flory-Huggins
Hydrogen-fluoride EOS for hexamerisation[1]	Scatchard-Hildebrand
Ideal gas law[1]	UNIQUAC
Lee-Kesler	UNIFAC
Lee-Kesler-Plöcker	Van Laar
Peng-Robinson	Wilson
Perturbed-Hard-Chain	
Predictive Soave-Redlich-Kwong	Special Models
Redlich-Kwong (RK)	API sour-water method
Soave-Redlich-Kwong (SRK)	Braun K-10
SRK or RK with Wong-Sandler mixing rule	Chao-Seader
SRK or RK with modified-Huron-Vidal-2 Mixing rule	Grayson-Street
	Kent-Eisenberg
Sanchez-Lacombe for polymers	Stream Tables

[1]not used for liquid phase

A.2.2. Binary Input Parameters (BIPs)

Liquid mixing properties properties were calculated using the NRTL model. The model is given by:

$$\ln \gamma_1(x_1,T) = (1-x_1)^2\left[\tau_{21}(T)\left(\frac{G_{21}(T)}{x_1+(1-x_1)G_{21}(T)}\right)^2 + \tau_{12}(T)\frac{G_{12}(T)}{\left((1-x_1)+x_1G_{12}(T)\right)^2}\right] \quad \text{(A-1)}$$

$$\ln \gamma_2(x_1,T) = x_1{}^2\left[\tau_{21}(T)\left(\frac{G_{12}(T)}{(1-x_1)+x_1G_{12}(T)}\right)^2 + \tau_{21}(T)\frac{G_{21}(T)}{\left(x_1+(1-x_1)G_{21}(T)\right)^2}\right] \quad \text{(A-2)}$$

where:

$$G_{ij}(T) = \exp\left(-\alpha_{ij}\tau_{ij}(T)\right) \quad \text{(A-3)}$$

$$\tau_{ij}(T) = A_{ij} + \frac{B_{ij}}{T} \quad \text{(A-4)}$$

$$\alpha_{12} = \alpha_{21} \quad \text{(A-5)}$$

Five parameters are needed to calculate the activity coefficients, namel A_{ij}, A_{ji}, B_{ji}, B_{ij} and α_{ij}

Table A.4.2. Binary Input Parameters (BIPs) [°C]

Comp i	Comp j												
	PROP	FORMIC	ACETIC	WATER	DEK	ETH-ACET	MEK	ME-ACET	ACETONE	ETHANOL	ME-FORM	ACETALDE	METHANOL
METHANOL	2.5	2.5	2.5	1.55	1.2112	1.3	1	1.3	1	1.55	0.5569	0.8	1.63
ACETALDE	1.6	1.6	1.6	0.8	0.7225	0.75	1	0.75	1	0.8	0.3407	0.58	
ME-FORM	0.9489	0.9489	0.9489	0.5832	0.4244	0.3257	0.4124	0.4124	0.4244	0.5569	0.2001		
ETHANOL	2.5	2.5	2.5	1.55	1.1225	1.3	1	1.3	1	1.4			
ACETONE	1.8	1.8	1.8	1	0.9	1.1	0.9	1.1	0.9				
ME-ACET	2	2	2	1.3	0.8746	0.53	1.1	0.85					
MEK	1.8	1.8	1.8	1	0.9	1.1	0.9						
ETH-ACET	2	2	2	1.3	0.6907	0.53							
DEK	2.0125	2.0125	2.0125	1.2369	0.9								
WATER	2.5	4.499	2.5	1.7									
ACETIC	4.5	4.5	4.5										
FORMIC	4.5	4.5											
PROP	4.5												

Table A.4.3. NRTL-1 Binary Interaction Parameters Input Measured in [°C]

Comp i	Comp j	aij	aji	bij	bji	cij
METHANOL	ACETALDE	0.0	0.0	3.1398223	-284.7856	0.3
METHANOL	ME-FORM	0.0	0.0	108.84522	322.71939	0.3
METHANOL	ETHANOL	0.0	0.0	0.1031995	0.0217351	0.3
METHANOL	ACETONE	0.0	0.0	128.0175	89.5663	0.3
METHANOL	ME-ACET	0.0	0.0	139.5156	214.4191	0.3
METHANOL	MEK	0.0	0.0	208.81267	69.795301	0.3
METHANOL	ETH-ACET	0.0	0.0	153.81296	214.36757	0.3
METHANOL	DEK	0.0	0.0	-79.5281	480.8318	0.3
METHANOL	WATER	2.636	-2.892	-921.01	1315.88	0.47
METHANOL	ACETIC	-3.8591	7.4858	975.377	-2151.8792	0.3
METHANOL	FORMIC	0.0	0.0	-288.10883	457.26402	0.3
METHANOL	PROP	-3.5108	6.5966	676.1322	-1280.1602	0.3
ACETALDE	ME-FORM	0.0	0.0	425.10854	-260.11734	0.3
ACETALDE	ETHANOL	0.0	0.0	-264.46611	364.78337	0.3
ACETALDE	ACETONE	0.0	0.0	615.06157	-363.29866	0.3
ACETALDE	ME-ACET	0.0	0.0	521.55224	-318.34208	0.3
ACETALDE	MEK	0.0	0.0	203.97676	-171.78356	0.3
ACETALDE	ETH-ACET	0.0	0.0	-321.31694	442.22028	0.3
ACETALDE	DEK	0.0	0.0	286.76501	-179.1094	0.3
ACETALDE	WATER	16.9	-1.1	-4629.0205	566.6537	0.3
ACETALDE	ACETIC	0.0	0.0	695.3864	-3014208	0.3
ACETALDE	FORMIC	0.0	0.0	497.79445	-37.436838	0.3
ACETALDE	PROP	0.0	0.0	601.61466	-285.21372	0.3
ME-FORM	ETHANOL	0.0	0.0	305.6293	183.1835	0.3
ME-FORM	ACETONE	0.0	0.0	440.8291	-302.9901	0.3
ME-FORM	ME-ACET	0.0	0.0	552.45291	-344.75215	0.3
ME-FORM	MEK	0.0	0.0	457.15441	-292.83085	0.3
ME-FORM	ETH-ACET	0.0	0.0	604.40405	-361.096	0.3
ME-FORM	DEK	0.0	0.0	463.28522	-248.42415	0.3
ME-FORM	WATER	0.0	0.0	-21.844358	506.41708	0.3
ME-FORM	ACETIC	0.0	0.0	1087.2927	-648.30664	0.3
ME-FORM	FORMIC	0.0	0.0	241.64981	-50.775275	0.47
ME-FORM	PROP	0.0	0.0	1086.2651	-648.68808	0.3
ETHANOL	ACETONE	0.0	0.0	153.59561	63.598694	0.3
ETHANOL	ME-ACET	0.0	0.0	216.0415	115.0684	0.3
ETHANOL	MEK	-1.5767	0.6538	664.1577	-106.4792	0.3
ETHANOL	ETH-ACET	0.0	0.0	106.76002	209.6136	0.3

Comp i	Comp j	aij	aji	bij	bji	cij
ETHANOL	DEK	0.0	0.0	179.2592	142.7384	0.3
ETHANOL	WATER	-0.9852	3.7555	302.2365	-676.0314	0.3
ETHANOL	ACETIC	0.0	0.0	212.0418	-229.79502	0.3
ETHANOL	FORMIC	0.0	0.0	-187.83513	630.99951	0.3
ETHANOL	PROP	0.0	0.0	281.2317	-383.8709	0.3
ACETONE	ME-ACET	0.0	0.0	1.9382392	40.147727	0.3
ACETONE	MEK	-0.2901	0.1841	448.2809	-319.14	0.3
ACETONE	ETH-ACET	0.0	0.0	160.72	-92.9	0.3
ACETONE	DEK	0.0	0.0	-250.3474	353.0698	0.3
ACETONE	WATER	-2.65	7.767	1111.81	-2073.75	0.3
ACETONE	ACETIC	0.0	0.0	772.98	-437.99	0.3
ACETONE	FORMIC	0.0	0.0	208.0961	80.983095	0.3
ACETONE	PROP	0.0	0.0	757.54682	-445.42711	0.3
ME-ACET	MEK	0.0	0.0	-18.5818	34.9343	0.3
ME-ACET	ETH-ACET	-5.1693	1.0457	1988.7587	-526.6985	0.3
ME-ACET	DEK	0.0	0.0	79.2863	56.9984	0.3
ME-ACET	WATER	0.0	0.0	279.76958	834.31201	0.3
ME-ACET	ACETIC	0.0	0.0	710.0032	-371.2695	0.3
ME-ACET	FORMIC	0.0	0.0	1006.9551	-451.3030	0.3
ME-ACET	PROP	0.0	0.0	692.08298	-337.80799	0.3
MEK	ETH-ACET	0.0	0.0	-104.073	170.3103	0.3
MEK	DEK	0.0	0.0	-253.7151	336.1477	0.3
MEK	WATER	0.0	0.0	193.1265	1095.4507	0.3
MEK	ACETIC	0.0	0.0	544.662	-284.6987	0.3
MEK	FORMIC	0.0	0.0	58.694241	-118.08482	0.3
MEK	PROP	0.0	0.0	428.5936	-265.3154	0.3
ETH-ACET	DEK	0.0	0.0	334.9233	-231.4131	0.3
ETH-ACET	WATER	0.0	0.0	661.0442	1212.1603	0.47
ETH-ACET	ACETIC	0.0	0.0	515.8212	-235.2789	0.3
ETH-ACET	FORMIC	0.0	0.0	333.80456	256.7866	0.3
ETH-ACET	PROP	0.0	0.0	653.20796	-316.58936	0.3
DEK	WATER	0.0	0.0	504.9479	1217.8649	0.3
DEK	ACETIC	0.0	0.0	439.173	-159.5488	0.3
DEK	FORMIC	0.0	0.0	36.524297	814.585	0.3
DEK	PROP	0.0	0.0	570.2167	-319.1397	0.3
WATER	ACETIC	0.0	0.0	541.3	-146.83	0.3
WATER	FORMIC	0.0	0.0	368.37	-368.4	0.3
WATER	PROP	0.0	0.0	999.54	-161.17	0.3

Comp i	Comp j	aij	aji	bij	bji	cij
ACETIC	FORMIC	0.0	0.0	149.83746	-53.859524	0.3
ACETIC	PROP	0.0	0.0	-239.47	310.85	0.3
FORMIC	PROP	0.0	0.0	-70.07	268.55	0.3

A.2.3. Comparison of simulation results with experimental data

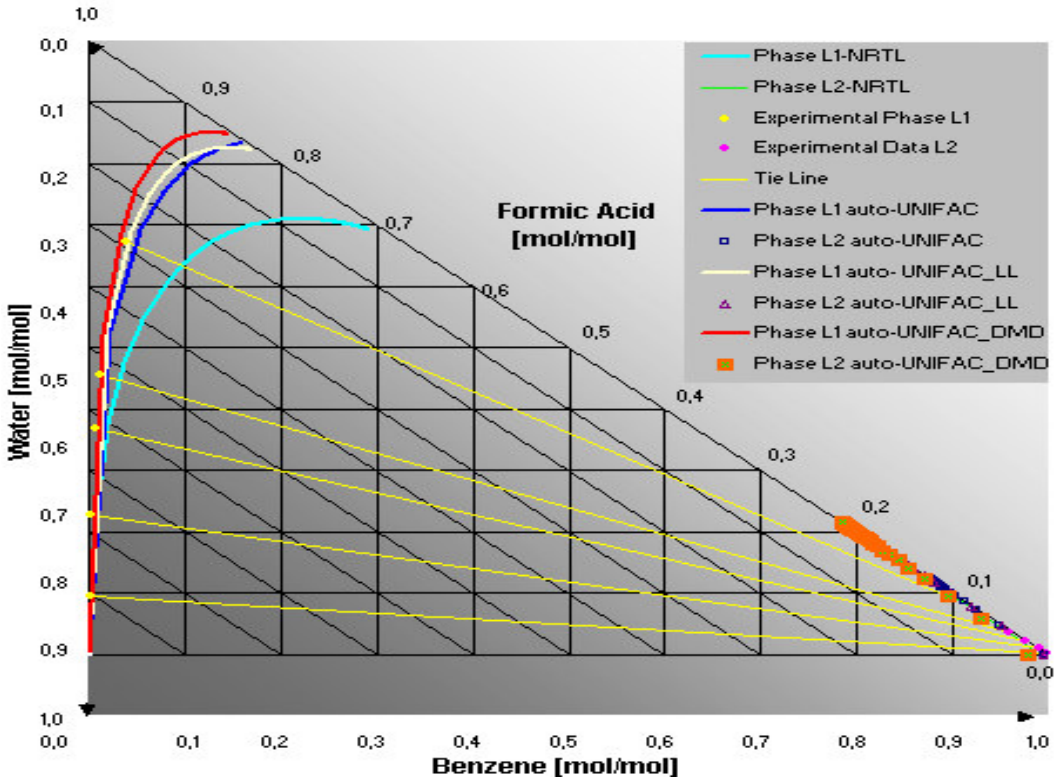


Figure A.2.3.1. Automatic Regression of ASPEN Plus BIPs.

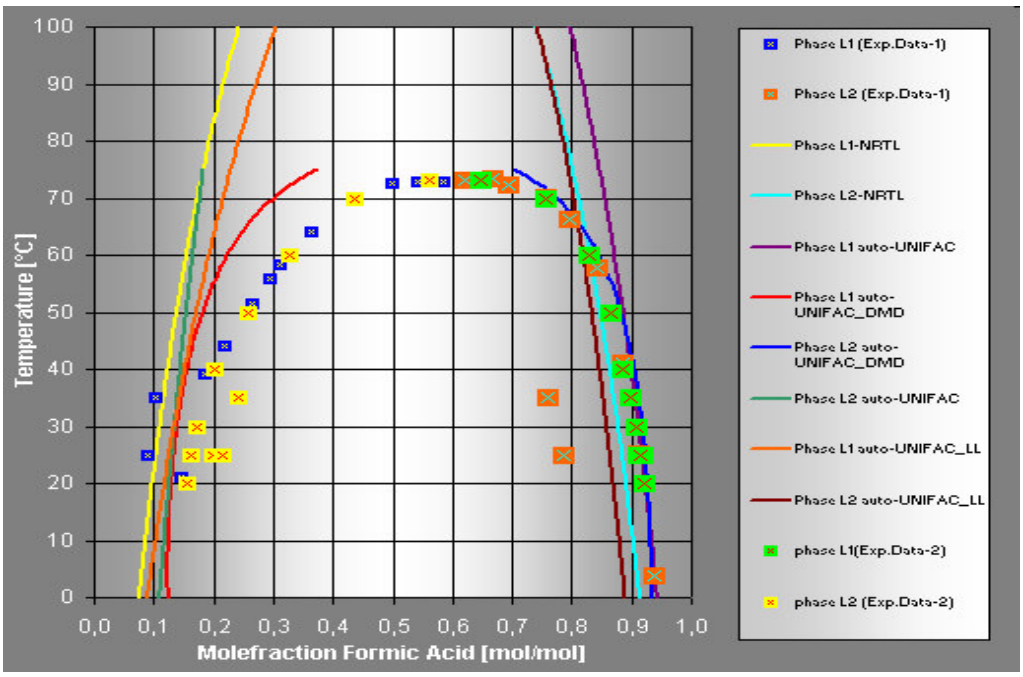


Figure A.2.3.2. Automatic regression of Benzene-Formic Acid binary subsystem

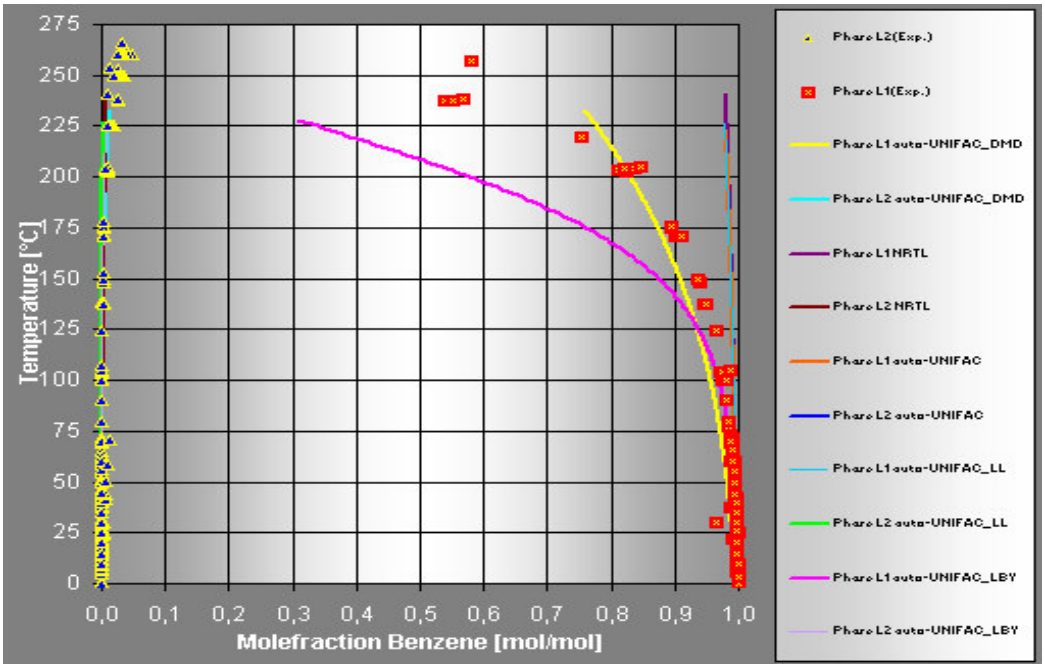


Figure A.2.3.3. Automatic regression Benzene - Water binary subsystem

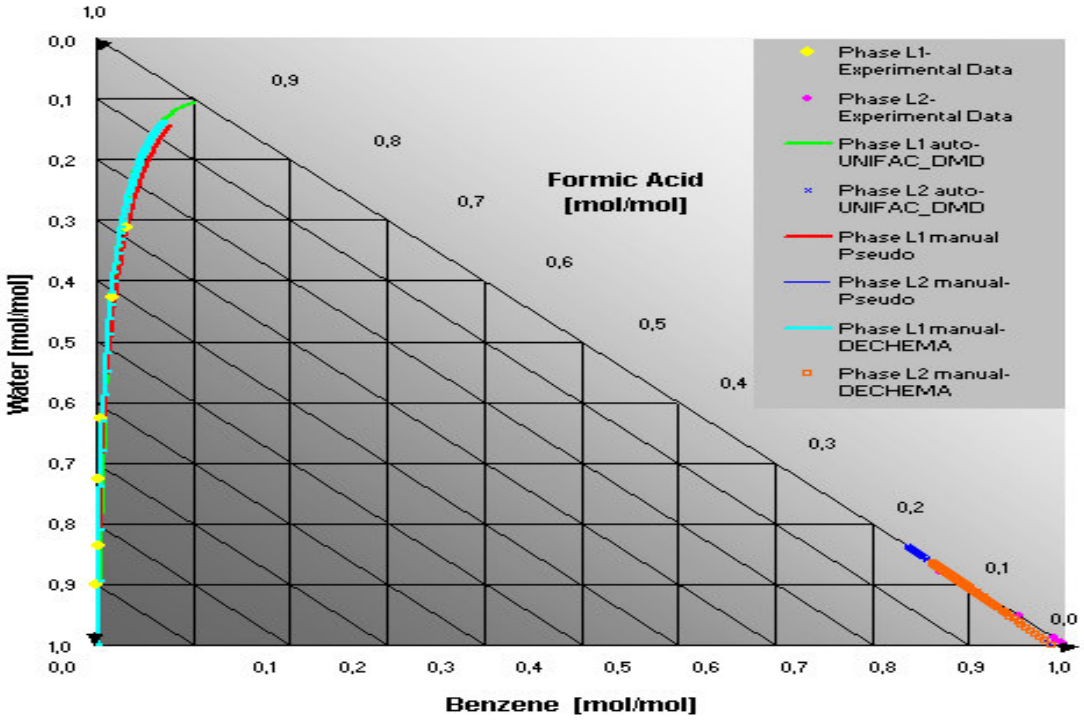


Figure A.2.3.4. Comparison between automatic regression and manual regression

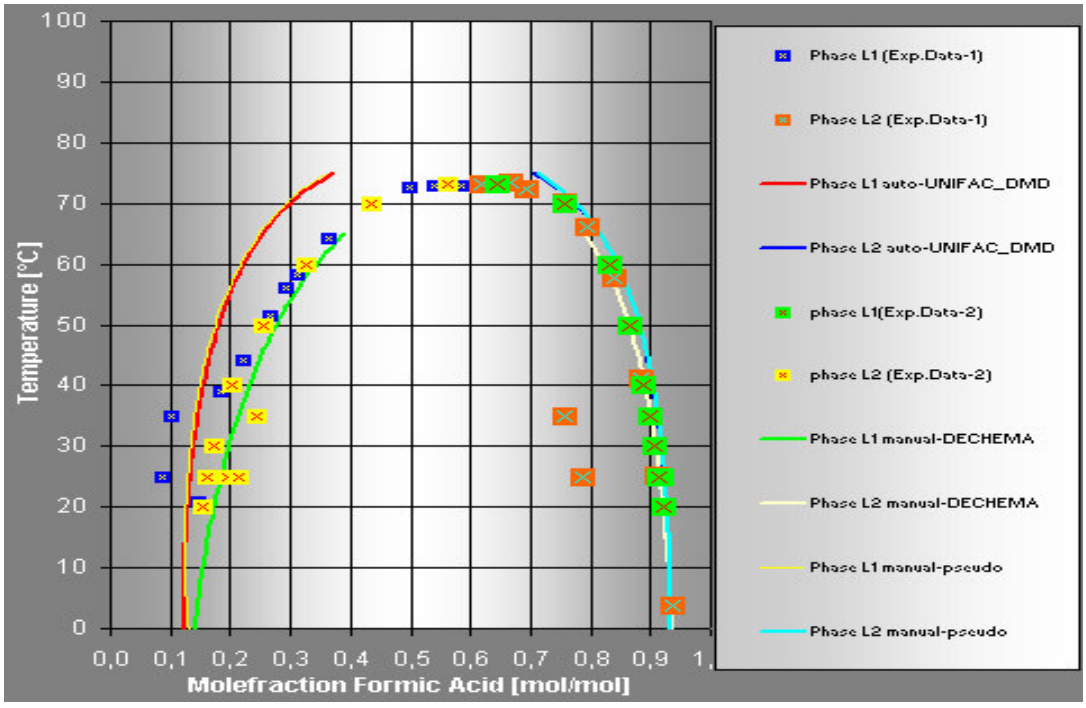


Figure A.2.3.5. Automatic regression of binary subsystem

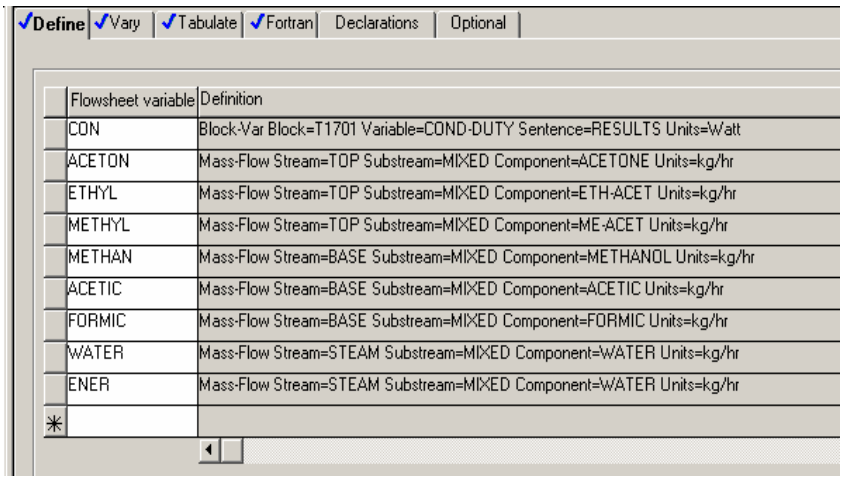
A.3. Sensitivity and Optimisation Forms in ASPEN Plus

A.3.1. Important Terms in Engineering Design

The discussion toward engineering optimisation always starts from the explanation of the variables that are dealt with. These variables might adjust/ modify to obtain expected design. The following important terminologies are used for the problem of formulation in engineering design:

- Independent design variable, that is variables that are dealt with directly that express the actual quantities, e.g. geometry, material properties, production volume, etc. These variables are also called as design variables or design parameters for simplification.
- Dependent variable, that cannot directly assign and designer work with them through design parameters. These variables represent the characteristics or attributes of the design, or a function of the characteristics of the design.
- Objective function is the relation between design parameters and particular design characteristics. However, for general design problems, it might be difficult to represent the relation analytically since the characteristics are the outcome of complex simulation.
- State variable, that is an intermediate design between dependent and independent design variables.
- Operating variable, that is variables that can be changed after the design has been built.

With the aid of ASPEN Plus, only block input and process feed stream variables may be varied. Furthermore, ASPEN Plus can specify up to five varied variables. Once a variable with units has been selected, these units are displayed on this sheet. This form is also possible to specify values, or a range of values, for the varied variables. One row of the table is generated for each possible combination of varied variable values. The number of possible combinations can be surprisingly large, resulting in excessive computer time and storage requirements. For example, 10 points for each of the maximum of five varied variables would result in 100,000 evaluations of the sensitivity block loop and approximately 2,000 pages of report output.



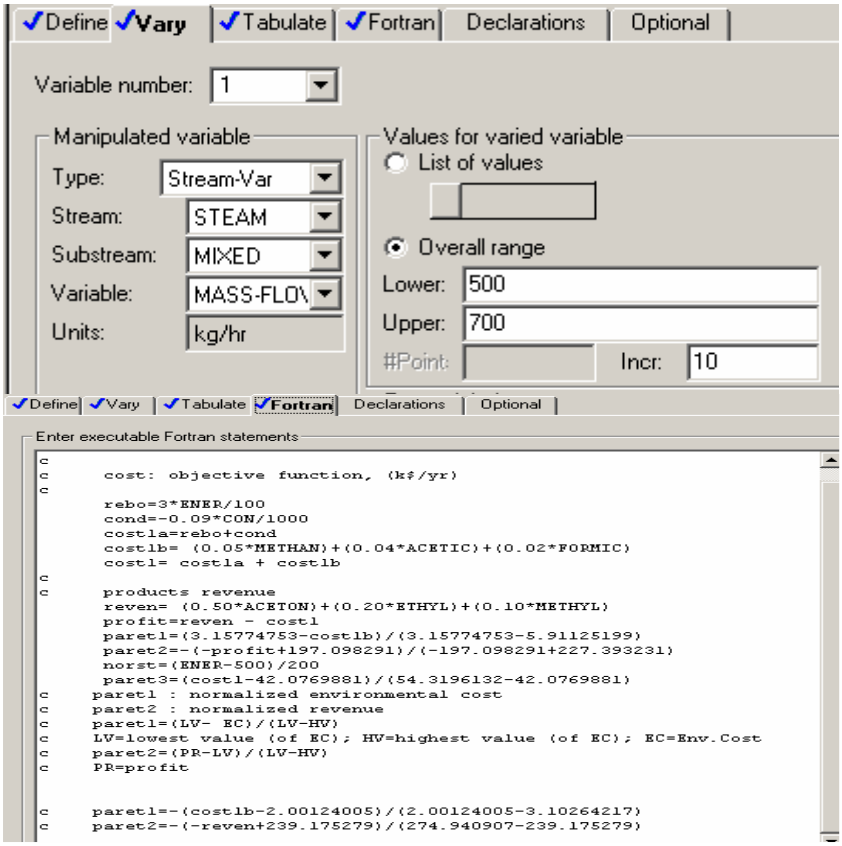


Figure A.3.1. Example of variables definition in ASPEN Plus Flowsheet

A.3.2. Formulation

Objective function :

- Minimisation of operating cost (k$/yr)
- Maximisation of profit (k$/yr)

Utility Cots:

- Cost for heat source: from steam:
- Cost for cooling water in condenser.
- Total utility costs = steam cost + cooling water cost

A.4. Waste Reduction Algorithm

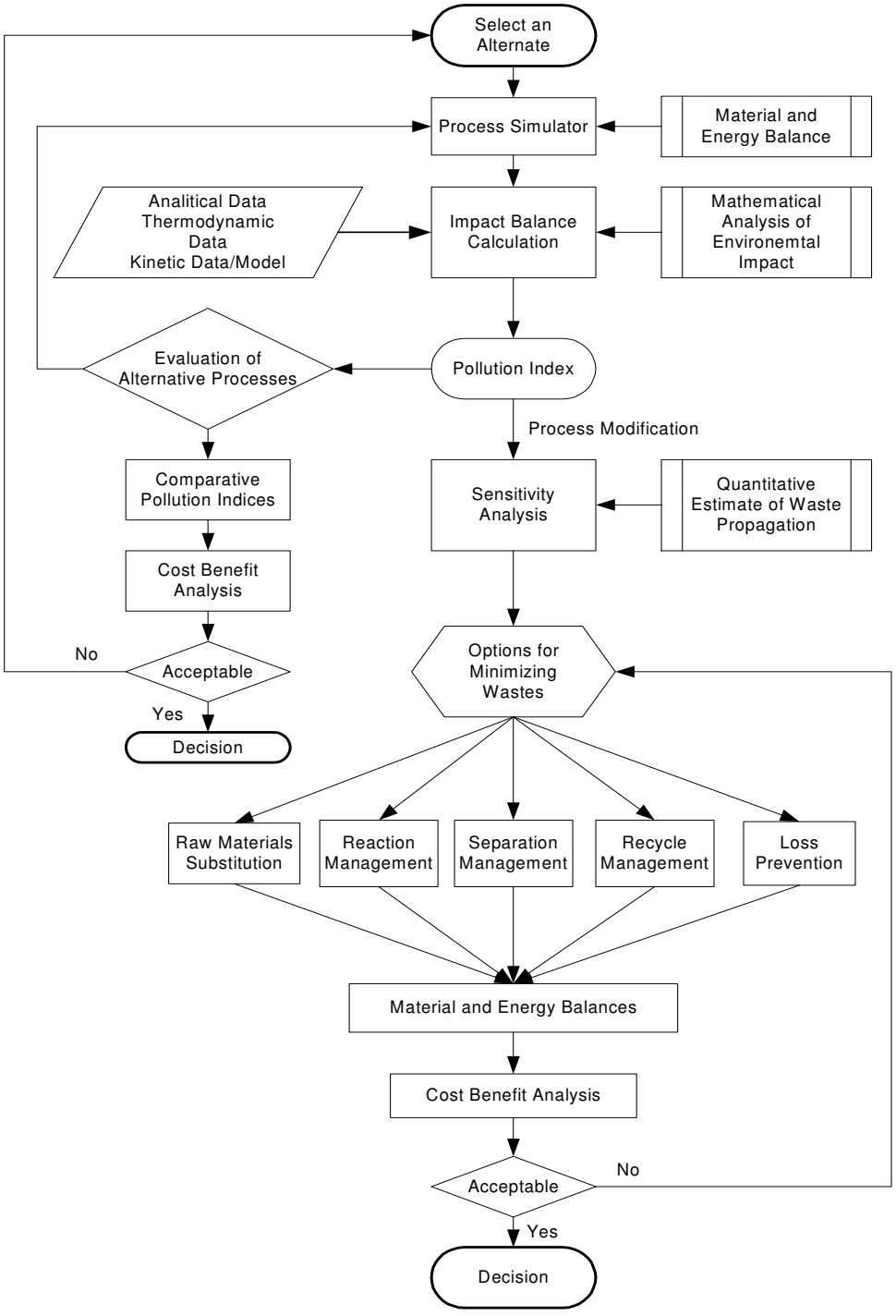


Figure A.4.1. Flow diagram of waste reduction algorithm